福井大学審査

学位論文　[博士（工学)]

Degradation of hazardous organic compounds using ultrasound techniques

（超音波法による有害有機化合物分解に関する研究）

2008 年 3 月

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“*Auf jeden Regen folgt auch Sonneschein”*
German proverb

CONTENTS

CHAPTER 1
General introduction

Sonochemistry is a field involving the application of ultrasounds to chemical processing and recently, has been widely investigated due to its benefits. Ultrasounds enhances or promotes chemical reactions and mass transfer; offers potential for shorter reaction cycles, cheaper reagents and less extreme physical conditions, leading to inexpensive and smaller plants [1]. Nowadays sonochemistry is utilized in several areas including production of nanomaterials, food technology, electrochemistry, reactor design, therapeutic ultrasound and environmental protection, especially in water and land remediation and sewage treatment. Although sonochemical techniques can be considered a very suitable method for the degradation of organic compounds, there is still a lack in research that explain the degradation mechanisms correlating them to the production of radicals which are the fundamental tool of the sonochemistry. This thesis intends to fill this lack, focusing on the degradation of three different hazardous organic compounds using sonochemical reactions, and explaining about their physical and chemical parameters.

1.1 Fundamentals of ultrasound

Ultrasounds are waves at frequencies higher than 16 kHz that are inaudible for humans [2]. The ultrasonic irradiation to liquids at these high frequencies generates cavitation bubbles which grow during compression/rarefaction cycles until they reach a critical size, and implode generating heat and highly reactive radical species [3]. Fig. 1-1 shows the process of formation and collapse of the transient cavitation bubble. Inside the cavitation bubbles, temperature and pressure rise to the order of 5000 K and 100 MPa, respectively, as shown in Fig. 1-2.

These extreme conditions are very short-lived but result in the generation of highly reactive species including hydroxyl radical and hydrogen peroxide, as shown by equations (1-1) to (1-8):

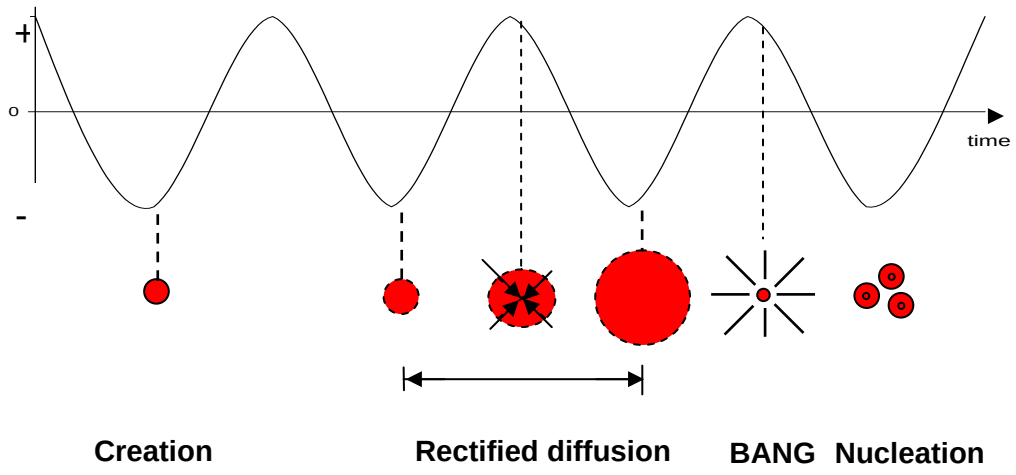

Fig 1-1 Process of formation and collapse of the transient cavitation bubble.

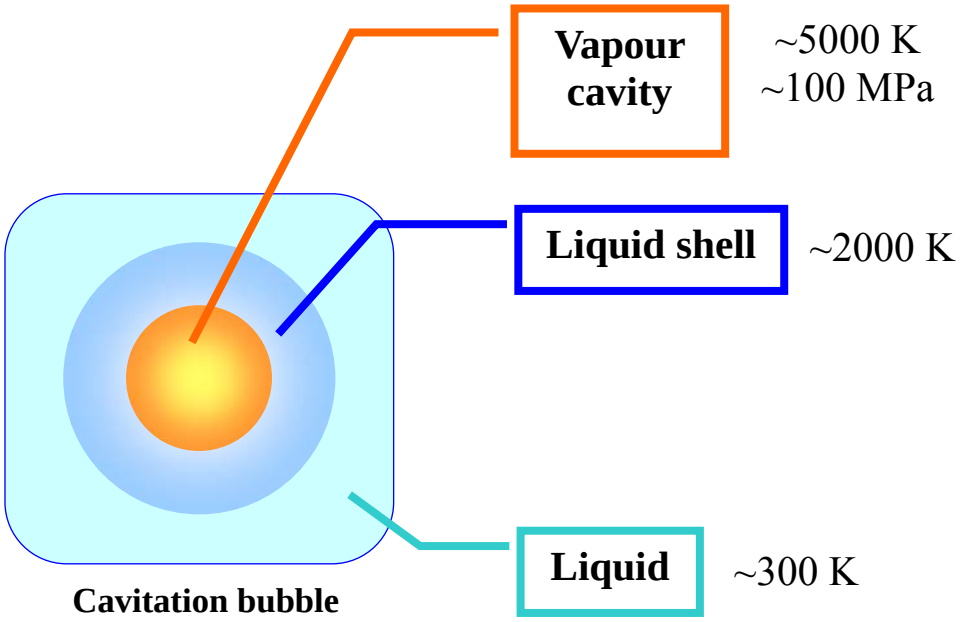

Fig. 1-2 Cavitation bubble immediately prior to collapse.

$$H_2O \rightarrow H\bullet + OH\bullet \quad (1\text{-}1)$$
$$H\bullet + OH\bullet \rightarrow H_2O \quad (1\text{-}2)$$
$$2H\bullet \rightarrow H_2 \quad (1\text{-}3)$$
$$2OH\bullet \rightarrow H_2O_2 \quad (1\text{-}4)$$
$$2OH\bullet \rightarrow O\bullet + H_2O \quad (1\text{-}5)$$
$$2O\bullet \rightarrow O_2 \quad (1\text{-}6)$$
$$O\bullet + 2H\bullet \rightarrow H_2O \quad (1\text{-}7)$$
$$O\bullet + H_2O \rightarrow H_2O_2 \quad (1\text{-}8)$$

Inside the bubble or in the liquid shell surrounding the cavity, these radicals can combine in various ways or react with the gases and vapor present, leading to the detection of H_2O_2, HNO_2 and HNO_3 in the medium, as shown by equations (1-9) to (1-14)[4]:

$$N_2 \rightarrow 2N\bullet \quad (1\text{-}9)$$
$$O_2 \rightarrow 2O\bullet \quad (1\text{-}10)$$
$$N\bullet + O\bullet \rightarrow NO \quad (1\text{-}11)$$
$$NO + O\bullet \rightarrow NO_2 \quad (1\text{-}12)$$
$$OH\bullet + NO \rightarrow HNO_2 \quad (1\text{-}13)$$
$$OH\bullet + NO_2 \rightarrow HNO_3 \quad (1\text{-}14)$$

These radicals can oxidize the solute occasioning its degradation. By the means of the attack of OH radicals to solute compounds, the degradation of pollutants can be carried out in an ecological process, without release of any kind of side products just like the sludge formed during some biological degradation processes [5]. Several studies have been made in order to investigate the viability of the ultrasonic waves in degradation of hazardous organic compounds or focused the optimization of the sonochemical parameters such as ultrasonic frequency, ultrasonic intensity, reactions environment and so on. As the ultrasonic degradation is based on the availability of the free radicals, a suitable way to increase their concentration in solution is also desirable. It can be achieved by the addition into the solution of Fenton and Fenton-like reagents, which can react with the H_2O_2 produced by the combination of free radicals, increasing thus the availability of OH radicals in solution, optimizing the degradation process itself.

1.2 Uses of ultrasound

Several studies involving the use of sonochemical processes to treat a variety of chemical contaminants in aqueous systems have been made. Sonochemical processes were used to degrade, for example:

- aromatic compounds;
- organic dyestuffs;
- chlorinated aliphatic hydrocarbons.

Aromatic compounds [6,7]

The ultrasonic degradation of phenol, chlorophenols, and nitrophenols has been studied by a number of investigators. The intermediates and products of the sonochemical oxidation of phenol usually include hydroquinone, catechol, benzoquinone and some organic acids. Studies found that degradation occurs more rapidly at higher frequency (around 400 kHz). The sonodegradation of chlorophenols showed chlorohydroquinone, catechols, chlorocatechols and chlorides as intermediates and products. With addition of H_2O_2, the degradation rate increased substantially until a certain saturation value of H_2O_2 concentration. The dechlorination rates were also higher for frequencies around 500 kHz than 20 kHz. The products found for nitrophenols degradation were nitrates, nitrites and organic acids, intermediates were nitrocatechols, hydroquinone and benzoquinone. High mineralization rates were found for higher ultrasonic frequencies.

Organic dyestuff

Studies found that dyestuff sonochemical degradation rates were substantially higher than the rates obtained by photocatalytical processes [6]. OH radicals formed during the cavitation phenomena attack the dyestuff molecules, destroying their chromophores, which are responsible for their color [8] and reducing the dyestuff solution TOC [9].

Chlorinated aliphatic hydrocarbons [6]

The sonochemical reactivity of chlorinated hydrocarbons in aqueous solutions is attributed to their volatility and their low solubility in water, facilitating their concentration in the cavitation bubbles resulting in rapid degradation by high temperature and high pressure. In this case, the degradation occurs mainly by thermal degradation in the cavitation bubbles and not reactions with the OH radical. Some

products found for trichloroethylene degradation were: chloroacetylene, dichloroacetylene, dichlorodiacety- lene, tetrachloroethylene, trichlorobutenyne, tetrachlorobutenyne, pentachlorobutadiene and hexachlorobutadiene. Degradation was more efficient around 500 kHz than 20 kHz.

1.3 References

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CHAPTER 2
Degradation of dyestuffs using sonochemical reactions

2.1 Introduction

Among the many organic compounds found in wastewaters, the pollution caused by dyestuffs has been a serious environmental problem for years. Synthetic dyestuffs are used extensively by several industries; the worldwide annual production of dyestuffs is over 7×10^5 tons and it is estimated that 10 to 15% of the dyestuff is lost in the effluent during the dyeing processes. Some azo dyestuffs and their reaction products are carcinogenic. Thus, the treatment of the effluents containing such compounds is important for the protection of waters and the environment in general [1].

The treatment of wastewater -containing dyestuffs by conventional methods such as flocculation, air sparging and activated carbon adsorption is quite ineffective for the decolorization of wastewater since dyestuffs are difficult to remove using these processes due to their low molecular weight and high water solubility [2]. Other processes, such as coagulation and adsorption, merely transfer the pollutant from the wastewater to other media that produce sludge and cause disposal problems [3].

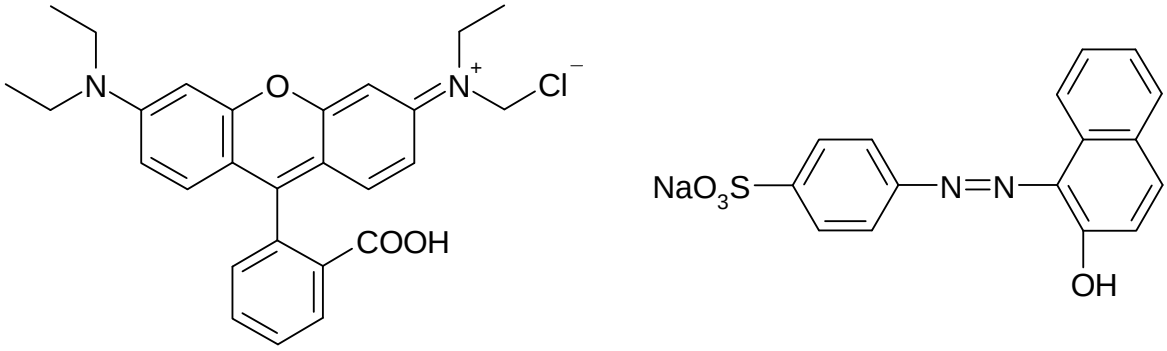
In the past years, sonochemistry has emerged as an advanced oxidation process for the destruction of hazardous organic compounds in aqueous solutions due to the high reactivity of the radicals formed during the ultrasonic irradiation to solutions. These radicals react with the solute molecules, causing their degradation and consequently their detoxification, without the use of many reagents and complex apparatus as occur with other methods.

This chapter shows the use of sonochemical reactions to degrade Rhodamine B (basic dye) and Orange II (azo dye); utilizing frequencies in the range of 118 to 651 kHz and ultrasonic intensities from 3.5 to 12.9 kW/m^2, verifies the influence of the ultrasonic frequency and intensity on dyestuff degradation processes; and correlates the degradation efficiency with the formation of H_2O_2, HNO_2 and HNO_3.

2.2 Materials and methods

2.2-1 Chemicals

Rhodamine B and Orange II were purchased from Wako Pure Chemicals Industries, Ltd., Japan. Fig. 2-1 shows the chemical structures of these dyestuffs. Hydrogen peroxide was supplied by Sigma-Aldrich Japan, Ltd.. All other reagents were of commercially available analytical grade.



Rhodamine B **Orange II**

Fig. 2-1 Chemical structures of Rhodamine B and Orange II.

2.2-2 Ultrasonic system

The degradation experiments were carried out in a cylindrical jacketed stainless steel reactor (ϕ 64 × 108 mm) equipped with a 400 kHz type piezoelectric ceramic transducer, made by Honda Electronics Co., Ltd., Japan. The ultrasonic power was supplied by a high frequency amplifier (L-400 BM-H, Tokyo HY-Power Lab., Inc., Japan) through a multifunction synthesizer (WF 1943, NF Electronics Instruments Co., Japan), and the temperature was controlled at 25°C by a thermostat. The degradation reaction was conducted under air atmosphere. Fig. 2-2 shows a schematic diagram of the experimental apparatus, and Fig. 2-3 shows a photograph of the experimental apparatus.

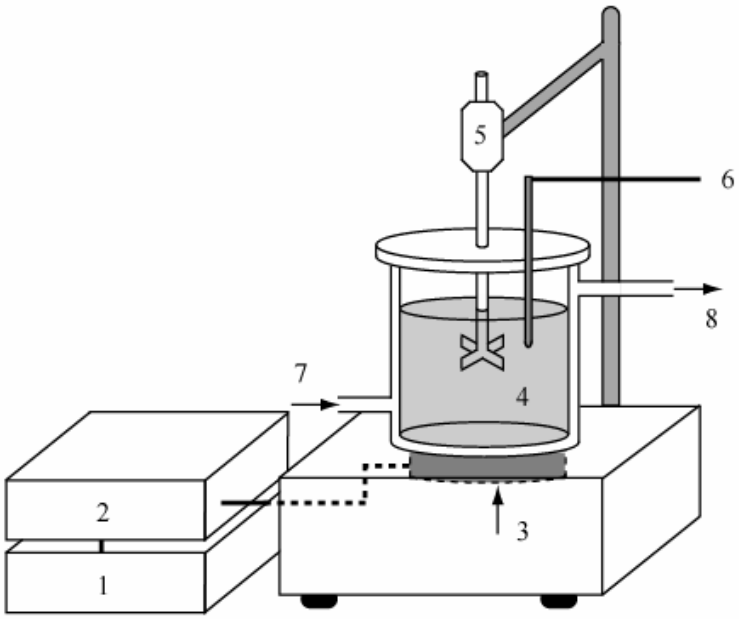


Fig. 2-2 Schematic diagram of the experimental apparatus.
(1) multifunction synthesizer, (2) amplifier; (3) transducer, (4) reactor, (5) stirrer, (6) temperature sensor, (7) cooling water inlet and (8) cooling water outlet.

Fig. 2-3 Photograph of the experimental apparatus.

2.2-3 Calorimetry

In order to verify the actual ultrasonic power, the energy dissipated by the apparatus was determined by calorimetry utilizing the equation (2-1). Input powers of 20, 40 and 60 W were tested, and the resulted actual powers were 11.4, 29.0 and 41.5 W, respectively. Fig. 2-4 shows a typical example of the graph utilized to determine the actual power. As the ultrasonic efficiency also depends on the irradiated surface, in this work, the values of ultrasonic intensity were used in place of the actual power. The ultrasonic intensity was defined as the actual power divided by the area of the transducer. The intensity values found for the actual powers of 11.4, 29.0 and 41.5 W were 3.5, 9.0 and 12.9 kW/m^2, respectively.

$$Power\,(W) = \frac{dT}{dt} \cdot c_p \cdot m \qquad (2\text{-}1)$$

where, c_p = 4.2 J/(g ºC),

m = mass of water (g)

dT/dt = ºC/s

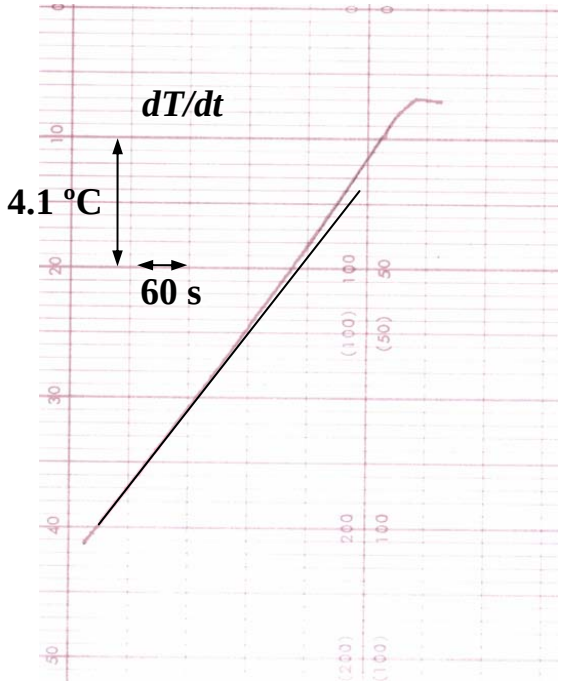


Fig. 2-4 Example of graph utilized to determine the actual power.

2.2-4 Analysis

Quantitative analysis of the hydrogen peroxide was carried out using a flow injection analyzer (BF-4, Oji Scientific Instruments, Ltd., Japan) at 37 ºC with a mobile phase of 0.2 M sodium dihydrogenphosphate 50% + 0.1 M potassium chloride 50% at the flow rate of 1.2 mL/min. The concentrations of the nitrous and nitric acids were determined using an ion chromatograph (LC-10A series with electroconductivity detector, Shimadzu Corp., Japan) under the following conditions: column temperature, 40 ºC; column type, IC-A3; mobile phase, 16.0 mM *p*-hydroxybenzoic acid 50%+ 6.4 mM Bis-Tris 50%; flow rate, 1.0 mL/min. The total organic carbon (TOC) analysis for 0 h and after 10 h of ultrasonic irradiation was performed using a TOC analyzer (TOC-5000A, Shimadzu Corp., Japan). The UV-visible spectrum for color removal was evaluated by a spectrophotometer (U-3200, Hitachi, Ltd., Japan).

2.2-5 Water degradation

Ultrasonics was used to irradiate 250 mL of air-saturated water for 10 h at frequencies of 118, 224, 404 and 651 kHz with intensity of 9.0 kW/m^2. Samples were taken at 30 min and at every hour to measure the pH and the concentrations of hydrogen peroxide, and the nitrous and nitric acids. Similar experiments were conducted by keeping the 404 kHz frequency constant and changing the ultrasonic intensity (3.5, 9.0 and 12.9 kW/m^2).

2.2-6 Dyestuff solutions degradation

Rhodamine B and Orange II solutions (250 mL, 25 mg/L) were prepared using air-saturated water. In order to determine the optimum frequency, these solutions were irradiated using ultrasounds at frequencies of 118, 224, 404 and 651 kHz for 10 h. The samples were taken at 30 min and at every hour, and the pH and the concentrations of hydrogen peroxide, and the nitrous and nitric acids were determined. Absorbance of these samples were determined at 545 nm for the Rhodamine B solution or 485 nm for the Orange II solution, and additionally, the samples at 0, 15, 45 and 90 min were also measured. Similar experiments were conducted at the frequency of 404 kHz and changing the ultrasonic intensity (3.5, 9.0 and 12.9 kW/m^2). In these cases, the

concentrations of the dyestuffs were 50 mg/L. The TOC values were measured at the irradiation times of 0 and 10 h.

2.3 Results and discussion

2.3-1Effect of the ultrasonic frequency

Water degradation

In the case of water degradation, the hydrogen peroxide, and the nitrous and nitric acid concentration plots for 10 h of ultrasonic irradiation are shown in Figs. 2-5a and b. While the system with the ultrasonic frequency of 118 kHz had low concentrations of both hydrogen peroxide and nitric acid, the systems using the ultrasonic frequencies from 224 to 651 kHz showed curves very similar one to another, but the 404 kHz system, at the end of the reaction, exhibited a slightly higher concentration for hydrogen peroxide (26.2 mg/L). Comparing the data in Fig. 2-5a with other studies, the hydrogen peroxide concentration found by Pétrier et al. [5] for 1 h of ultrasonic irradiation at 487 kHz and 30 W and our data at 404 kHz and 29 W (9.0 kW/m^2, 1 h) not only have the same order but were very similar (9.5 mg/L and 7.5 mg/L, respectively). The hydrogen peroxide data reported by Nam et al. [10] using a 20 kHz system (19 W) for a 10 h ultrasonic exposure were about one-twentieth of our results using the 118 kHz system and about one-thirtieth of our results using systems in the range of 224 to 651 kHz, suggesting that the influence of the frequency on the ultrasound efficiency is an important factor for the optimization. Our results are also in agreement with Koda et al. [9] who suggested that the sonochemical effect caused by the sonolysis of water is most efficient at 200 to 500 kHz. The low efficiency at 118 kHz can be explained by the fact that the lifetime of the bubbles produced at low frequencies is longer and the production of radicals is slow, compared to systems using higher frequencies. The profiles of the nitric acid concentration for the systems in the range of 224 to 651 kHz shown in Fig. 2-5b were very similar, and after 10 h of ultrasonic irradiation, the nitric acid concentration reached about 140 mg/L. The nitric acid concentrations for 224 to 651 kHz were also comparable to those for 500 kHz reported by Nomura et al. [11]. In their

study, the concentration plots were linear within the given reaction time. For all the experiments, the concentration of nitrous acid was quite low; although, the nitrous acid was initially quite facilitated, it might react with hydrogen peroxide and be converted to nitric acid during the reaction. In all cases, the pH values were between 2.5 and 3.5 after 10 h of irradiation.

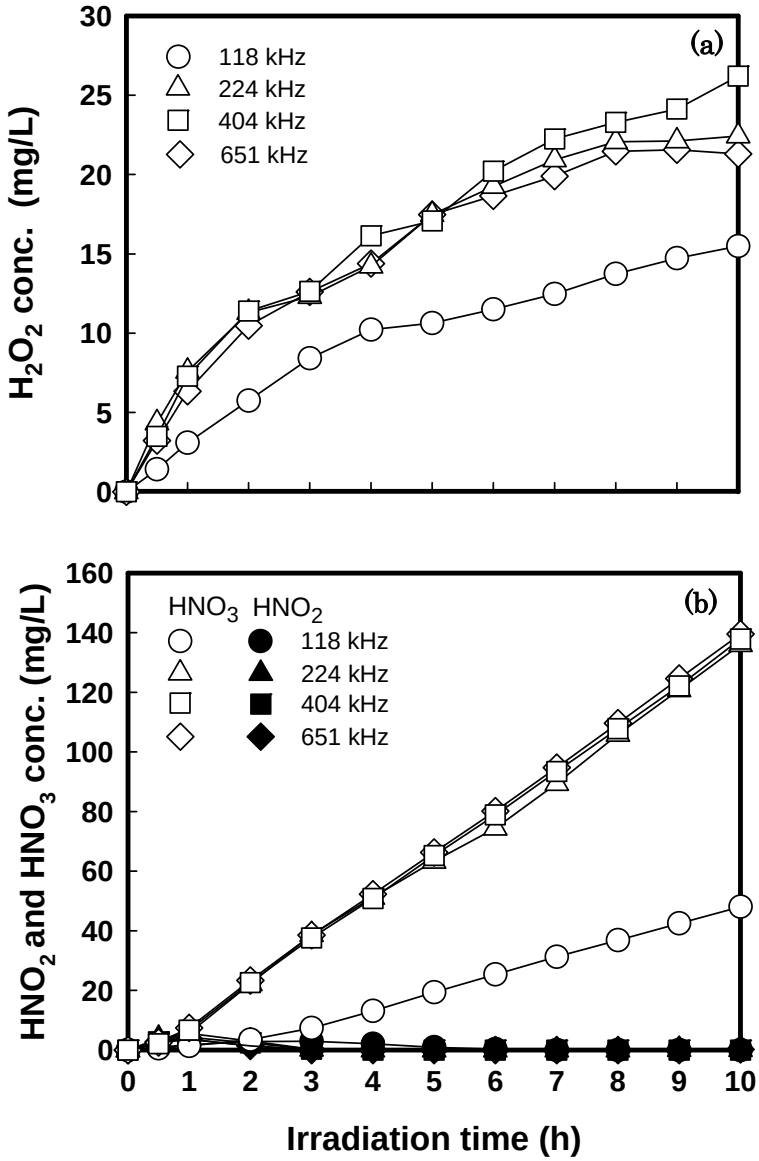


Fig. 2-5 Effect of ultrasonic frequency on H_2O_2, HNO_2 and HNO_3 formation during water degradation (ultrasonic intensity: 9.0 kW/m^2).

Dyestuff solutions degradation

In general, the hydrogen peroxide and nitric acid concentrations in the Rhodamine B and Orange II solutions during the ultrasonic irradiation were lower than those for water (data not shown). This is probably due to the consumption of some radicals for the dyestuffs degradation, resulting in fewer radicals for water degradation.

Analyzing the color removal of dyestuff solutions illustrated in Fig. 2-6, the Rhodamine B solutions decolorized within 2 h of ultrasonic irradiation for all cases

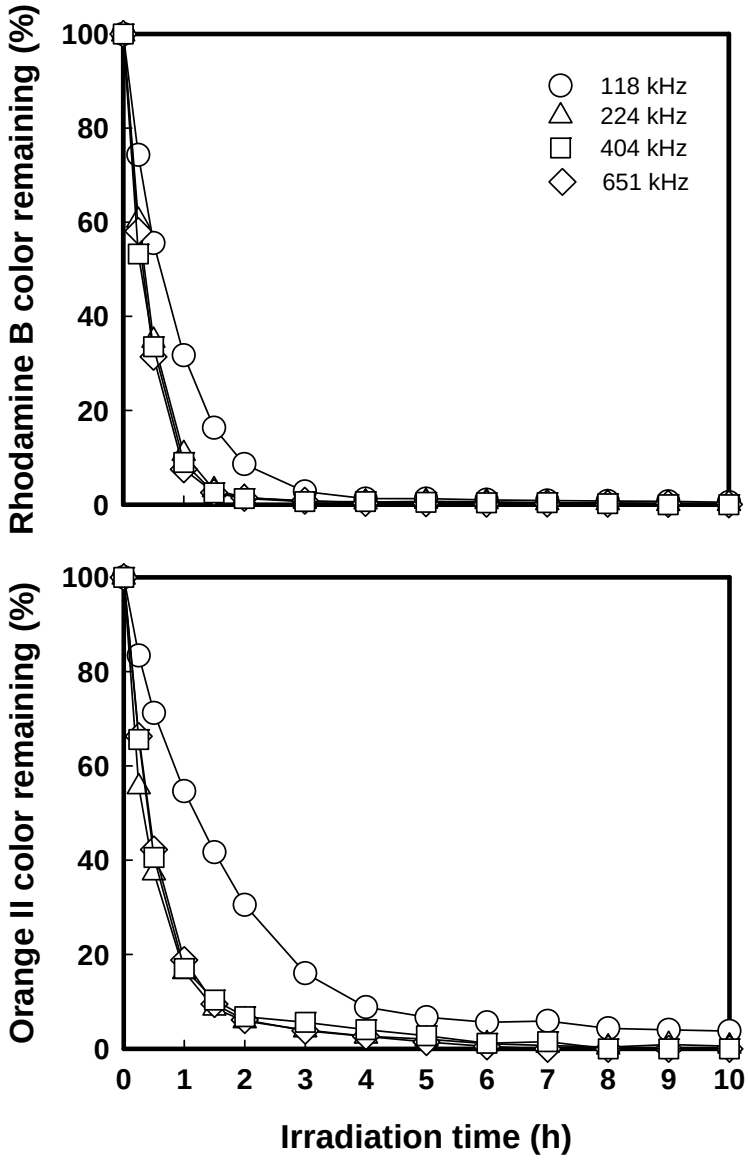


Fig.2-6 Effect of ultrasonic frequency on dyestuff color removal (ultrasonic intensity: 9.0 kW/m^2, dyestuff initial concentration: 25 mg/L).

except for the 118 kHz system. Similarly, for the Orange II solutions, all solutions excluding the 118 kHz case decolorized within 4 h. Even after 10 h of irradiation, the Orange II solution in the 118 kHz system was not completely decolorized.

2.3-2 Effect of the ultrasonic intensity

Water degradation

Ultrasonic systems ranging from 224 to 651 kHz showed similar data for the hydrogen peroxide, and nitrous and nitric acids concentrations after 10 h of ultrasonic irradiation. Therefore, being the intermediate frequency, the 404 kHz system was chosen as the basis for the experiments evaluating the effects of the ultrasonic input powers.

The effect of the ultrasonic intensity was verified by experiments using the intensities of 3.5, 9.0 and 12.9 kW/m^2 (corresponding to input power of 20, 40 and 60 W, respectively, as shown in the "Calorimetry" section). At first, the influence of the intensity was evaluated for water systems. Fig. 2-7 shows the plots for the hydrogen peroxide, and nitrous and nitric acid concentrations as a function of irradiation time.

The degradation of water in the system using 12.9 kW/m^2 showed a peak (27.4 mg/L) in the hydrogen peroxide concentration at 7 h of irradiation, indicating that probably the saturation point of hydrogen peroxide concentration in this system was reached at 7 h. The 3.5 and 9.0 kW/m^2 systems exhibited maximum concentrations (20.9 and 26.2 mg/L, respectively) at 10 h. Plots of the nitric acid concentrations as a function of the irradiation time showed almost a linear behavior with an increase in the ultrasonic power. The nitric acid formation was the highest for the 12.9 kW/m^2 system in which its concentration reached 250 mg/L after 10 h of irradiation. The nitrous acid formation was below 1 mg/L in all the systems.

Dyestuff solutions degradation

As mentioned in section 2.3-1, the results of the dyestuff solution degradations at frequencies from 224 to 651 kHz were very similar each other. In order to evaluate the influence of the ultrasonic power on the dyestuff solutions degradation, the frequency

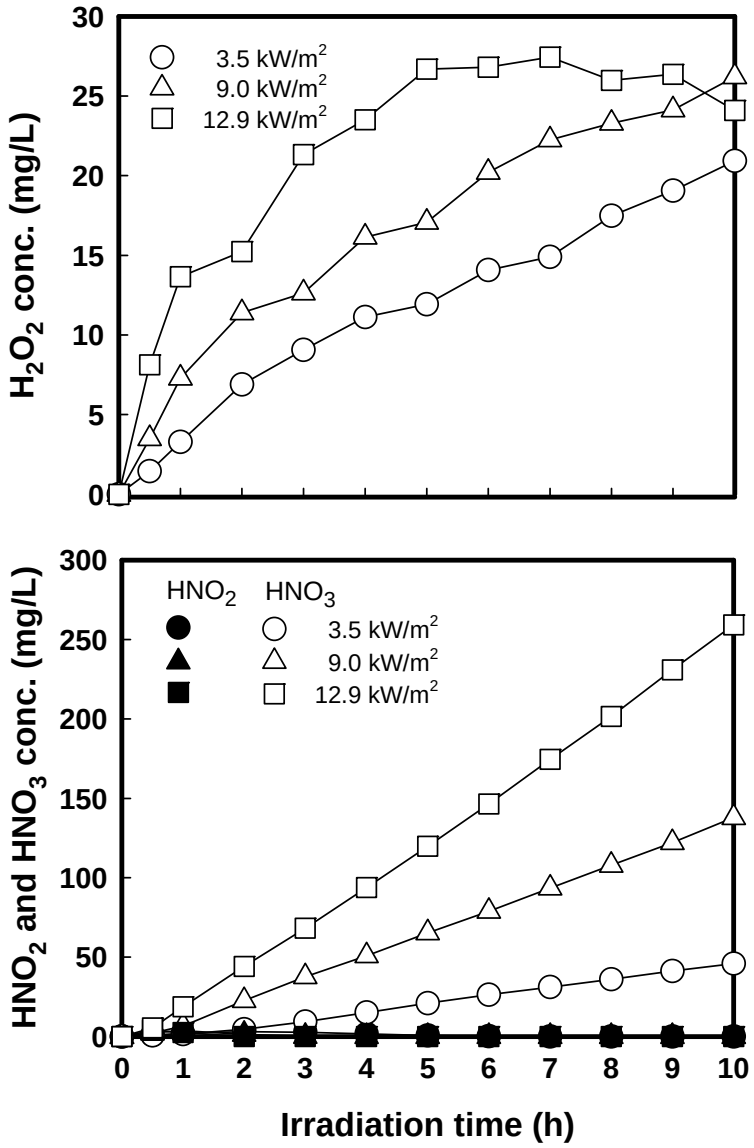


Fig. 2-7 Effect of ultrasonic intensity on H_2O_2, HNO_2 and HNO_3 formation during water degradation.

of 404 kHz was selected, and ultrasonic intensities of 3.5, 9.0 and 12.9 kW/m^2 were tested using the same procedures for the water degradation.

As Fig. 2-8 shows, the concentrations of hydrogen peroxide generated in the Rhodamine B and Orange II solutions were lower in all cases compared to water, because the produced radicals (for example OH•, H•) were probably utilized for the

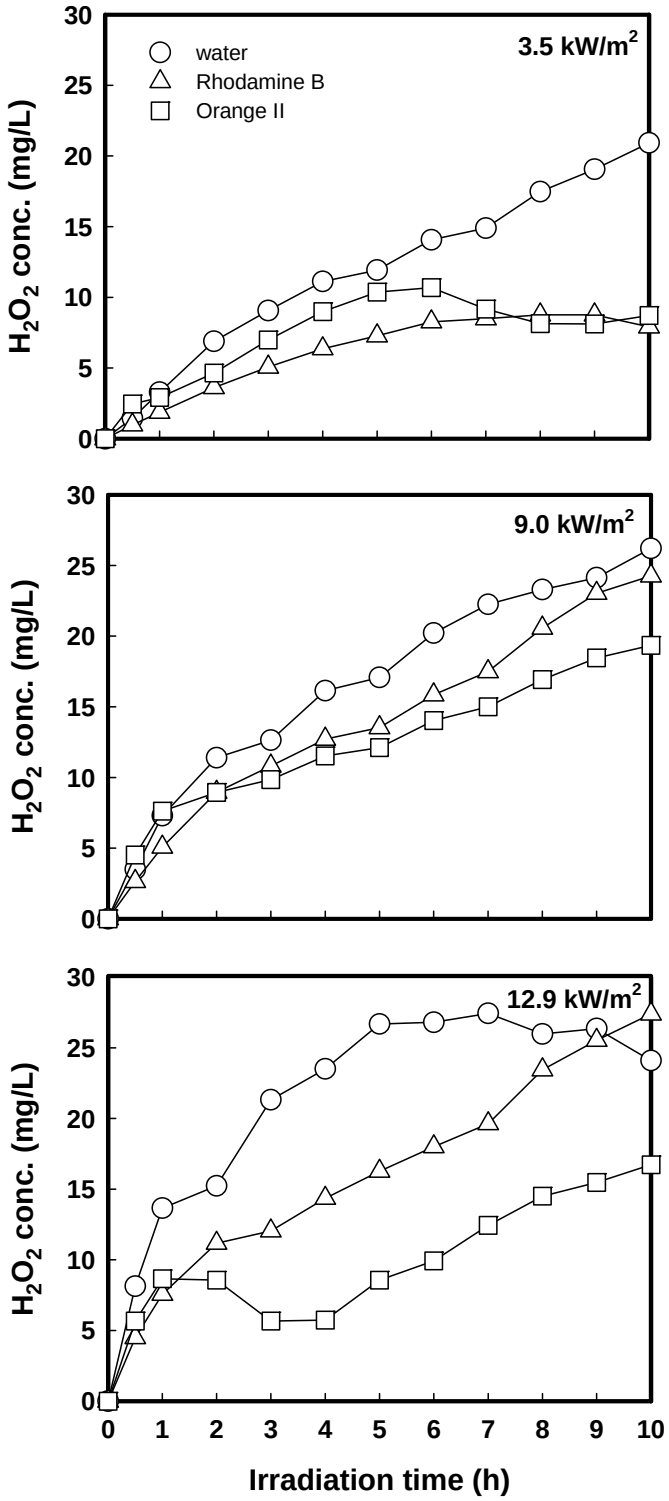


Fig. 2-8 Effect of ultrasonic intensity on H_2O_2 formation during water and dyestuff solution degradation (dyestuff initial concentration: 50 mg/L).

degradation of the dyestuffs. The three curves showed different behaviors, indicating that the ratio of the intermediates created may depend upon the ultrasonic power. Initially, the concentration of hydrogen peroxide is higher in the Orange II solutions compared to the Rhodamine B ones; proceeding the reaction, the concentration in Rhodamine B becomes higher. By increasing the ultrasonic power, this change in behavior tends to occur at an earlier irradiation time, most likely due to the different degradation mechanisms for Rhodamine B and Orange II.

As shown in Fig. 2-9, the curves of the nitric acid concentration found for the different solutions at each input power showed the same tendency.

The very low concentration of nitrous acid can be explained by the oxidation of nitrous acid to nitric acid by the hydrogen peroxide. Compared to the case for water, the concentration of nitric acid in the dyestuff solutions was lower, because similar to hydrogen peroxide, some of the radicals probably reacted with the dyestuffs during the degradation process. Furthermore, the nitric acid formation for Orange II was higher compared to Rhodamine B. One possible reason is the fact that the nitrogen content is higher in Orange II than in Rhodamine B, and it reacted to form nitrous acid and nitric acid in addition to the nitrogen from the air.

Fig. 2-10 shows the plots of the color removal for the Rhodamine B and Orange II solutions. Rhodamine B solution became colorless within 2 and 3 h of ultrasonic irradiation for the 12.9 kW/m^2 and 9.0 kW/m^2 cases, respectively. The orange II solution became colorless after 5 h (12.9 kW/m^2) and 9 h (9.0 kW/m^2). Even after 10 h, the 3.5 kW/m^2 system did not become completely colorless for both dyestuffs.

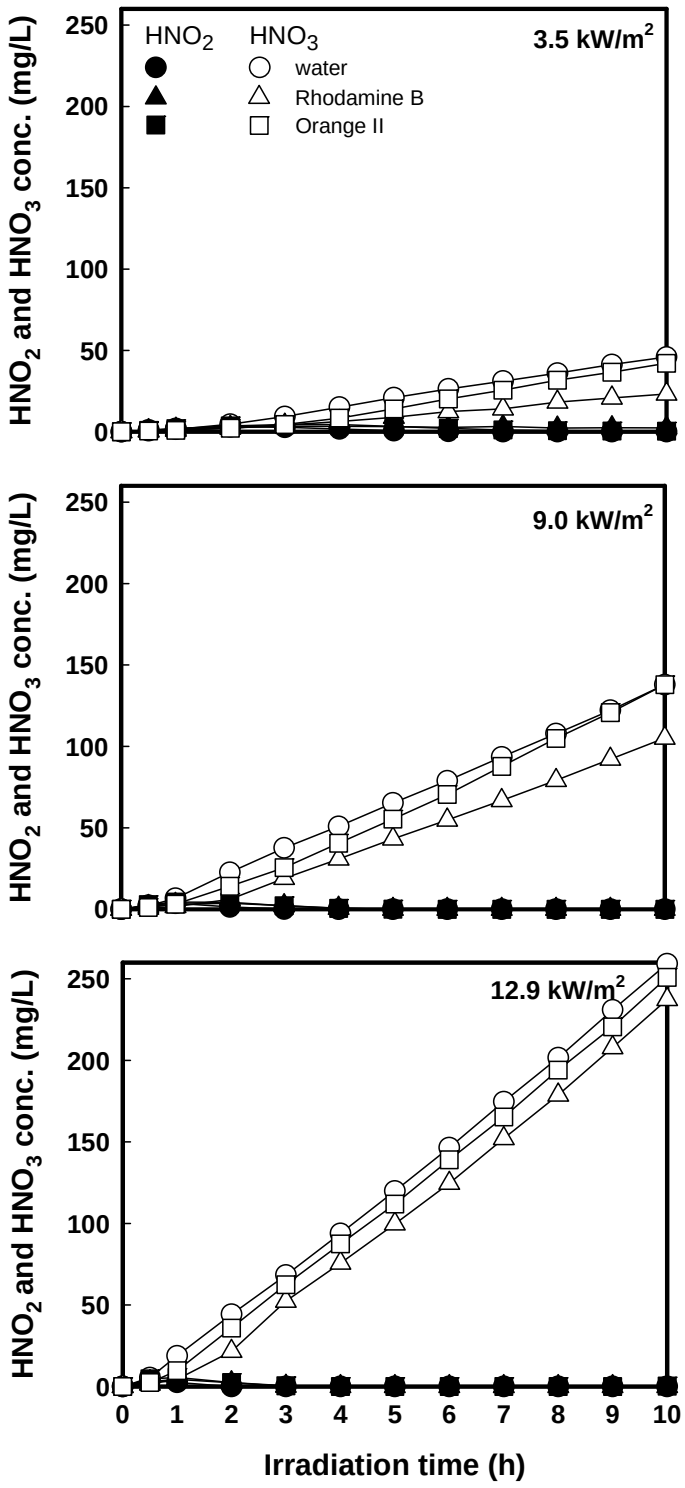


Fig. 2-9 Effect of ultrasonic power on HNO_2 and HNO_3 formation during water and dyestuff solution degradation (dyestuff initial concentration: 50 mg/L).

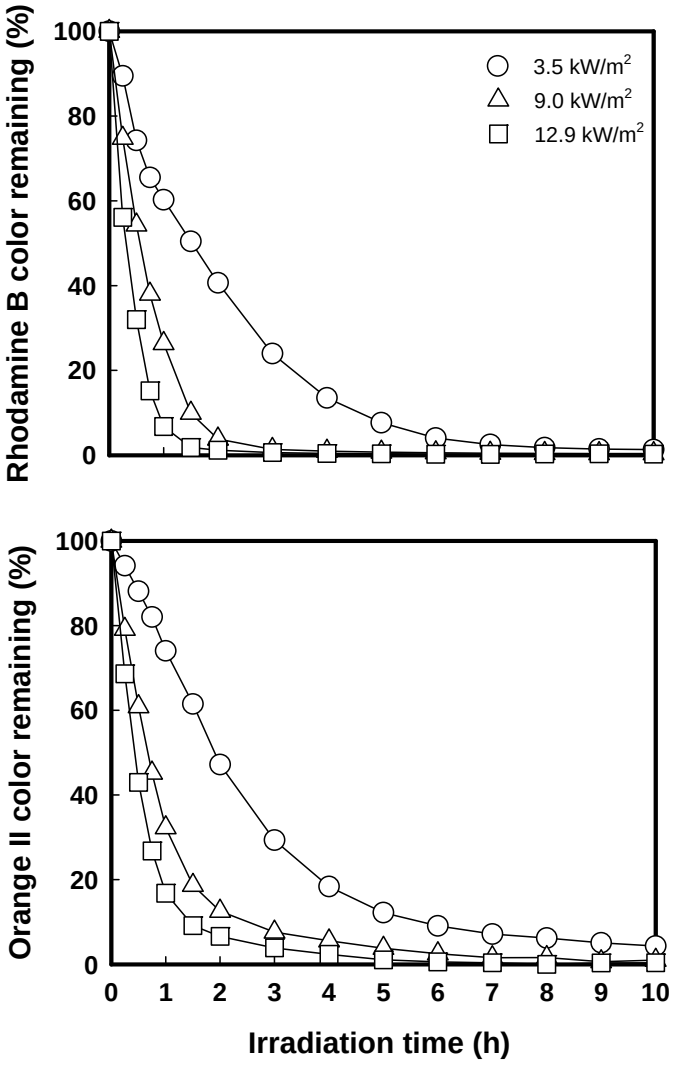


Fig. 2-10 Effect of ultrasonic intensity on dyestuff color removal (dyestuff initial concentration: 50 mg/L).

Table 2-1 Rate constant k for Rhodamine B and Orange II solutions

Intensity (kW/m^2)	k (1/s)	
	Rhodamine B	Orange II
3.5	1.3×10^{-4}	1.2×10^{-4}
9.0	4.0×10^{-4}	3.7×10^{-4}
12.9	7.4×10^{-4}	5.2×10^{-4}

From the initial degradation data for both dyestuffs solutions (0 to 1 h) in Fig. 2-10, the degradation rate constants were determined assuming pseudo first-order reaction kinetics [12]

$$\text{dyestuff}_{(aq)} + \text{OH}\bullet_{(aq)} \rightarrow \text{products} \tag{2-2}$$

where the rate constant *k'* can be determined by

$$-\frac{d[\text{dyestuff}]}{dt} = k'[\text{dyestuff}][\text{OH}\bullet] \tag{2-3}$$

as OH• is a very reactive species, it not only accumulates in solution, but its concentration takes on a steady-state value during the process. Therefore, equation (2-2) can be simplified, and *k'* takes the form of an apparent pseudo first-order constant *k*

$$-\frac{d[\text{dyestuff}]}{dt} = k[\text{dyestuff}] \tag{2-4}$$

For both dyestuff solutions, the rate constant *k* was highest for the 12.9 kW/m^2 system, followed by the 9.0 and 3.5 kW/m^2 systems as seen in Table 2-1. For the same input power, the Rhodamine B solution presented higher constants compared to the Orange II solution, indicating that the degradation of Rhodamine B is faster. This may be explained by the difference in the structural barriers and electrical localization based on the difference in their chemical structures.

The UV-visible spectra shown in Fig. 2-11 indicate that for both dyestuff solutions, chromophores peaks disappear after 10 h of ultrasonic irradiation. Similar spectra were also obtained by Ince et al. [13] who investigated azo dyestuffs. They indicated that the OH• radical, a priori, is added to the N=N or C–N bonds of the chromophores, in place of the aryl bonds. Rehorek et al. [14] found some intermediate products of the degradation of Acid Orange 52. Due to the similarity of the molecular structures of this dyestuff and Orange II, we can assume that Orange II solution degradation gives rise to similar products.

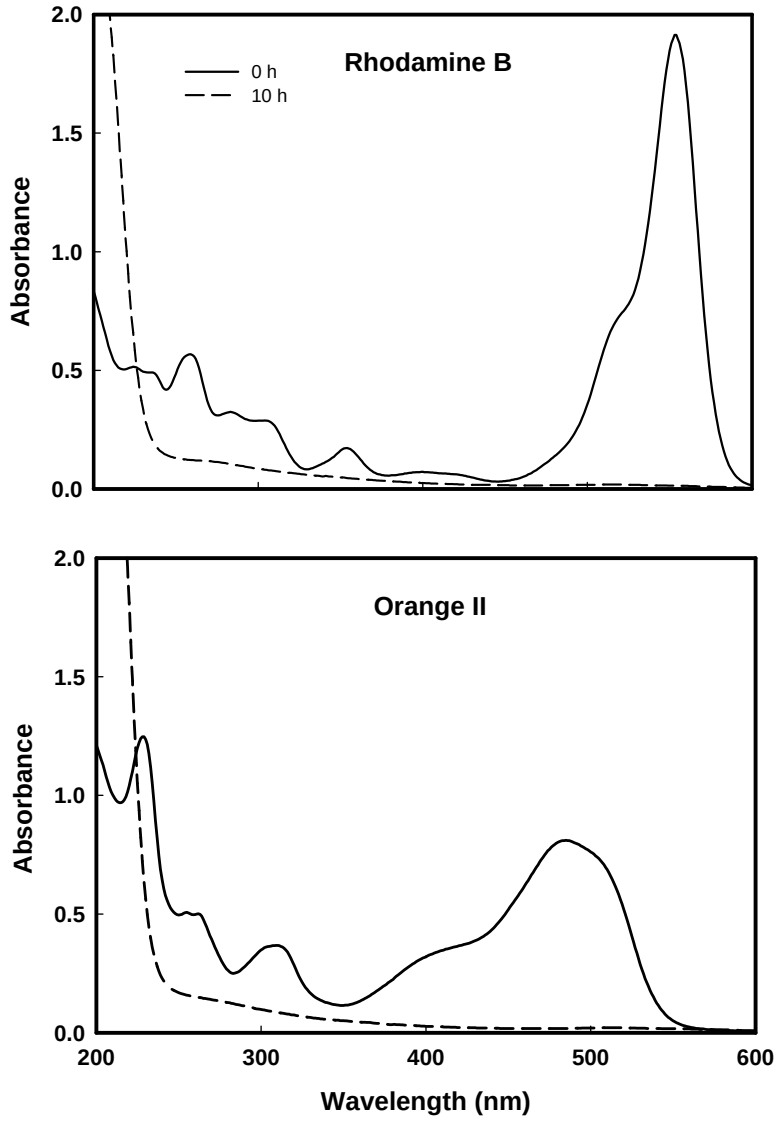


Fig. 2-11 UV-visible spectra for Rhodamine B and Orange II solutions for 0 and after 10 h of ultrasonic irradiation (404 kHz, 9.0 kW/m^2, dyestuff initial concentration: 50 mg/L). Dilution: Rhodamine B, 6 times; Orange II, 4 times.

Table 2-2 shows the mineralization percentages calculated from the TOC values. The frequency of 404 kHz provided better mineralization for both Rhodamine and Orange II. The best mineralization percentages for the Rhodamine B and Orange II systems using 12.9 kW/m^2 were 37.3 and 37.6 %, respectively. The TOC values showed that although a complete decolorization occurred in some cases, complete mineralization (conversion of all atoms of carbon to CO or CO_2) was not achieved because although the

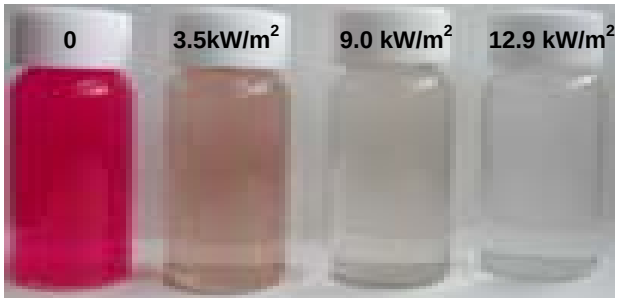
chromophores followed by the aromatic rings were broken by the ultrasonic irradiation (as shown in Fig. 2-11), organic carbons are partially remained in the degradation products as organic acids. Fig. 2-12 shows photographs of the dyestuff solutions before and after 10 hours of ultrasonic irradiation for all ultrasonic intensities. It can be observed that in both Rhodamine B and Orange II cases, the solutions become colorless in all cases except for the system using 3.5 kW/m^2 of ultrasonic intensity.

Table 2-2 Variation of TOC between 0 h and 10 h of ultrasonic irradiation

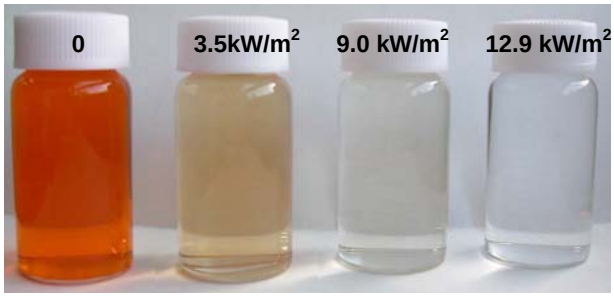
Dyestuff solution	frequency (kHz)	intensity (kW/m^2)	TOC [0 h] (mg/L)	TOC [10 h] (mg/L)	mineralization (%)
Rhodamine B	118	9.0	18.1	14.2	21.6
	224	9.0	17.0	11.3	33.5
	404	9.0	17.3	11.4	34.1
	651	9.0	17.2	11.6	32.6
	404	3.5	33.2	30.2	9.0
	404	9.0	35.1	27.5	21.7
	404	12.9	35.4	22.2	37.3
Orange II	118	9.0	13.1	12.6	3.8
	224	9.0	12.4	9.0	27.4
	404	9.0	12.8	8.9	30.5
	651	9.0	12.7	9.0	29.1
	404	3.5	26.0	24.1	7.3
	404	9.0	26.8	21.6	19.4
	404	12.9	26.1	16.3	37.6

Concerning the effect of ultrasonic frequency, the systems using frequencies from 224 to 651 kHz presented similar data for both hydrogen peroxide and nitric acid production, with slightly higher values provided by the 404 kHz system. The system using 118 kHz that produced only low quantities of hydrogen peroxide and nitric acid displayed the worst results.

For the case of different ultrasonic intensities, the system using 3.5 kW/m^2 showed low concentration of radicals, and consequently, low degradation rates. The 12.9 kW/m^2 system produced high degradation rates, however, the generation of hydrogen peroxide did not show a linear increase with the radical formation as the reaction proceeded. The 9.0 kW/m^2 system produced intermediate rates with a linear increase in the radical formations as the reaction proceeded.



Rhodamine B



Orange II

Fig. 2-12 Dyestuff solutions at 0 h and after 10 h of ultrasonic irradiation (404 kHz, dyestuff initial concentration 50 mg/L)

2.4 Summary

Concerning the effect of ultrasonic frequency, the systems using frequencies from 224 to 651 kHz presented similar data for both hydrogen peroxide and nitric acid production, with slightly higher values provided by the 404 kHz system. The system using 118 kHz that produced only low quantities of hydrogen peroxide and nitric acid displayed the worst results.

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CHAPTER 3
Degradation of hazardous phenols using sonochemical reactions

3.1 Introduction

Phenolic compounds are largely consumed in several kinds of industries, such as in the production of paints, textiles, plastics and medicines. These compounds are persistent in ground and river waters, and are a potential threat to human health and the environment. Most of them are resistant to conventional chemical treatments, and the traditional techniques employed to treat them, like adsorption [1], extraction [2] and flocculation [3] are not efficient considering that most of these methods only carried the pollutant from the liquid phase to other phases, not extinguishing the whole issue [4-5].

Recently, considerable interests have been focused on the application of sonochemical reactions for the destruction of hazardous compounds, including volatile organic compounds [6-9]. The degradation of chemical pollutants is possible through the effects of cavitation created by the irradiation of ultrasonic waves in liquids. By the cavitation phenomenon, the temperature and pressure rise to the order of 5000 K and 100 MPa. At such conditions, water molecules present inside the bubble degrade releasing OH and H radicals. These radicals can oxidize the solute occasioning its degradation [10]. In order to evaluate the efficiency of an ultrasonic system, it is extremely important to quantify the formation of these radicals. As OH radicals combine originating hydrogen peroxide, the quantity of hydrogen peroxide in solution can be correlated with the quantity of OH radicals available to take part in the degradation process. Traditional spectrophotometric methods to determine hydrogen peroxide concentrations using iodine as a reagent cannot be used for phenolic solutions because hydrogen peroxide may react with formed HNO_2 interfering in the absorbance and giving origin to analytical errors. In the present work, the analysis of hydrogen peroxide formation during phenol solution degradation was carried out by HPLC, using a method based on the quantitative analysis of the complex formed with Ti-5-BrPAPS and hydrogen peroxide.

Some efforts to improve the efficiency of the sonochemical reactions increase the

formation of OH radicals, facilitating the degradation. One of these efforts is the addition of the Fenton's reagent, which enhances the amount of OH radicals available in solution. The formation of OH radicals can be expressed by the equation (3-1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \qquad (3\text{-}1)$$

The radicals generated in the Fenton and Fenton like process have an oxidizing potential of 2.8 V vs. NHE (normal hydrogen electrode) and are capable of oxidizing wide range of organic compounds found in wastewaters [11-13]. Further increases in the concentration of Fe^{2+} showed no further catalytic activity, due to the direct reduction of OH radicals by the metal ions [14]:

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \qquad (3\text{-}2)$$

The present work verifies the influence of ultrasonic frequencies and intensities on the process of phenol solution degradation, identifies some of its intermediates and products, and confirms the effect of the presence of the Fenton's like reagent, correlating it to the formations of hydrogen peroxide, nitrous and nitric acid. Authors who focused on the degradation of phenol by ultrasonic waves, compared it to the formation of hydrogen peroxide during water degradation and [8, 15], but no data was found regarding the concentration of hydrogen peroxide present in the phenol solution during the degradation process. One of the reasons of this can be due to the difficulty to evaluate the concentration of hydrogen peroxide in phenol solution by traditional methods like iodometry.

3.2 Materials and methods

3.2-1 Chemicals

Phenol, $FeSO_4 \cdot 7H_2O$, 2-(5-bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl) amino]phenol (5-Br-PAPS), luminol, titanium and zephiramine were purchased from

Wako Pure Chemicals Industries, Ltd., Japan. Hydrogen peroxide was supplied by Sigma-Aldrich Japan, Ltd.. All other reagents were of analytical grade available commercially.

3.2-2 Ultrasonic system

The degradation experiments were carried out in a cylindrical jacketed stainless steel reactor (ϕ 64 × 108 mm) equipped with a Langevin or piezoelectric ceramics transducer (100 – 600 kHz), made by Honda Electronics Co., Ltd., Japan. The ultrasonic power was supplied by a high frequency amplifier (L-400 BM-H, Tokyo HY-Power Lab. Inc., Japan) through a multifunction synthesizer (WF 1943, NF Electronics Instruments Co., Japan), and the temperature (25°C) was controlled by a thermostat. Vide chapter 2, Fig. 2-2 for a schematic diagram of the experimental apparatus.

3.2-3 Calorimetry

The energy dissipated by the ultrasonic apparatus was determined by calorimetry and the values of the ultrasonic intensity were cited in Chapter 2, section 2.2-3.

3.2-4 Luminol reaction

Luminol reactions were carried out in an acrylic reactor with the same volume as the stainless steel reactor. Luminol solutions with a concentration of 0.1 g/L were prepared using 0.025 M of NaOH [16] and irradiated with ultrasonic waves for 5 min at 404 kHz and intensities of 3.5, 9.0 and 12.9 kW/m^2.

The photographs of the luminol reactions were taken with a digital camera Fine Pix 52 pro., made by Fuji Photo Film Co., Ltd., Japan; F 2.8; exposure time was 30 s.

3.2-5 Water and phenol solution degradation under ultrasonic irradiation

Phenol solutions (0.50 mM, 250 mL) were prepared using air saturated water and irradiated with ultrasonic waves for 10 h in the following experiments:

a) Using frequencies of 118, 224, 404 and 651 kHz with intensity of 9.0 kW/m^2.
b) Using intensities of 3.5, 9.0 and 12.9 kW/m^2 with a frequency of 404 kHz.

Samples were taken for every hour. Similar experiments were carried out with air saturated water in order to compare the formation of radicals in both phenol solution and water systems. The effect of the Fenton's like reagent was evaluated for solutions with the concentrations of 0.25, 0.50, 1.0, 2.0 and 4.0 mM of $FeSO_4$. Additional samples were taken at 15, 30 and 45 min to verify the kinetic of the degradation reactions.

3.2-6 Analytical procedures

The intermediate products of the phenol degradation were determined by comparison with fragments patterns of the Wiley library using a GC/MS analyzer (GC-MS QP5000, Shimadzu Corp., Japan) equipped with a VF-5ms capillary column (30 m × 0.25 mm i. d., Varian, Inc., USA) in helium carrier gas.

Quantitative analysis of phenol and derivates were carried out using the HPLC with a UV-visible detector (8020 series, Tosoh Corp., Japan) and a reverse phase column ODS-100S (Tosoh Corp., Japan) under the following conditions: wavelength, 270 nm; column temperature, 40°C; mobile phase, 0.1% phosphoric acid 75% + methanol 25% (vol.); flow rate, 0.75 mL/min. Concentrations of hydrogen peroxide were obtained by the following method: samples were reacted with Ti-5-Br-PAPS for 75 min at 40°C and the produced complex was analyzed in the HPLC with a UV-visible detector (8020 series, Tosoh Corp., Japan) and a reverse phase column Mightysil RP-18 GP (Kanto Chemical Co., Inc., Japan) under the following conditions: wavelength, 535 nm; column temperature, 40°C; mobile phase, acetonitrile 33% + 0.25 M sodium acetate 2% + 1 mM zephiramine 2% + distilled water 63% (wt); flow rate, 1.0 mL/min. Concentrations of nitrous, nitric and organic acids were determined using the ion chromatograph with an electroconductivity detector (10A series, Shimadzu Corp., Japan) under the following conditions: column type, IC-A3; column temperature, 40°C; mobile phase, 16.0 mM *p*-hydroxybenzoic acid 50% + 6.4 mM Bis-Tris 50% (wt); flow rate, 1.0 mL/min. The UV-visible spectrum was evaluated by a spectrophotometer (U-3200, Hitachi, Ltd., Japan). The total organic carbon (TOC) analysis was performed using a TOC analyzer (TOC-5000A, Shimadzu Corp., Japan).

3.3 Results and discussion

3.3-1 Effect of ultrasonic frequency on phenol solution degradation

Keeping the ultrasonic intensity constant (9.0 kW/m^2), experiments were carried out at frequencies of 118, 224, 404 and 651 kHz. Fig. 3-1 shows the decrease of phenol concentration for the four different frequencies. Although the phenol degraded completely after 10 h of ultrasonic irradiation in the case of 118 kHz, the other three frequencies showed a complete degradation of phenol after 4 h of irradiation. According to Koda et al. [17], who worked with KI oxidation and porphyrin derivatives decomposition, the most effective ultrasonic frequency for degradation purposes is in the range of 200-500 kHz.

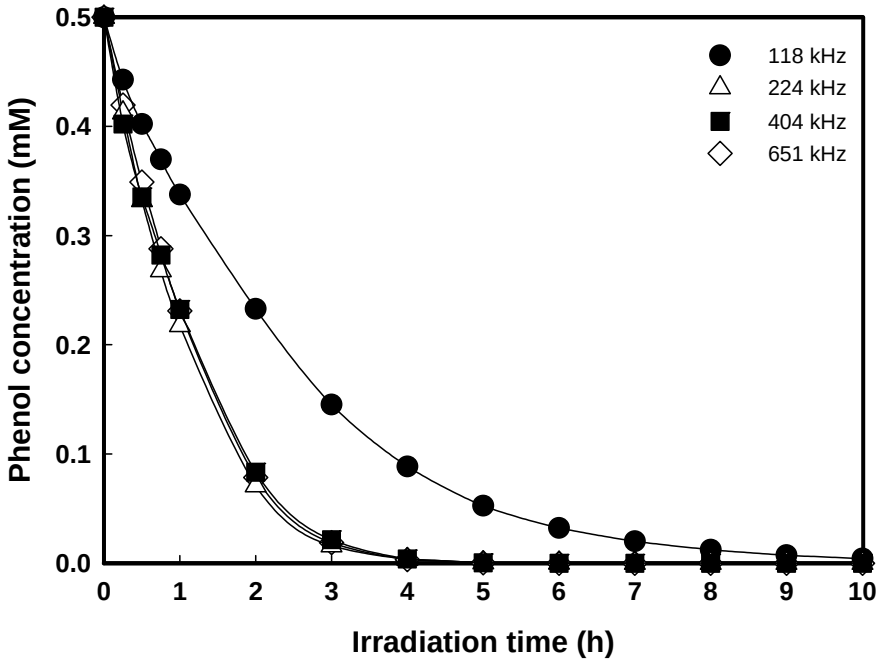


Fig. 3-1 Effect of ultrasonic frequency on phenol solution degradation (ultrasonic intensity, 9.0 kW/m^2; initial phenol conc., 0.50 mM).

For the first hour of ultrasonic irradiation, the initial degradation rate constants assuming pseudo first order reaction kinetics for each frequency were determined as 1.1 $\times$ 10^{-4}, 1.9 $\times$ 10^{-4}, 2.2 $\times$ 10^{-4} and 2.1 $\times$ 10^{-4} (1/s), respectively. Although the degradation

curves were very similar for the three higher frequencies, the frequency of 404 kHz showed a slightly higher degradation rate constant for the first hour of reaction.

3.3-2 Effect of ultrasonic intensity on phenol solution degradation

In order to verify the influence of the ultrasonic intensity on the phenol degradation process, the frequency of 404 kHz was kept constant, and experiments were carried out changing the ultrasonic intensity from 3.5 to 12.9 kW/m^2. For the systems with intensities of 3.5, 9.0 and 12.9 kW/m^2, the phenol disappeared after 8, 4 and 2 h of ultrasonic irradiation, respectively. Fig. 3-2 shows the UV-visible spectra for 0～10 h of phenol degradation at 404 kHz and 9.0 kW/m^2. It can be observed that there is an increase in the aromatic rings peak (around 270 nm) until 4 h of reaction and after that, the peaks decrease until 10 h of irradiation. It can be explained by the fact that for short irradiation time, there is a formation of intermediates with aromatic rings. After 4 h of reaction, aromatic rings cleavage occurs rapidly and at 10 h, the peaks decreased considerably. The absorbance at this time is due to the presence of organic acids.

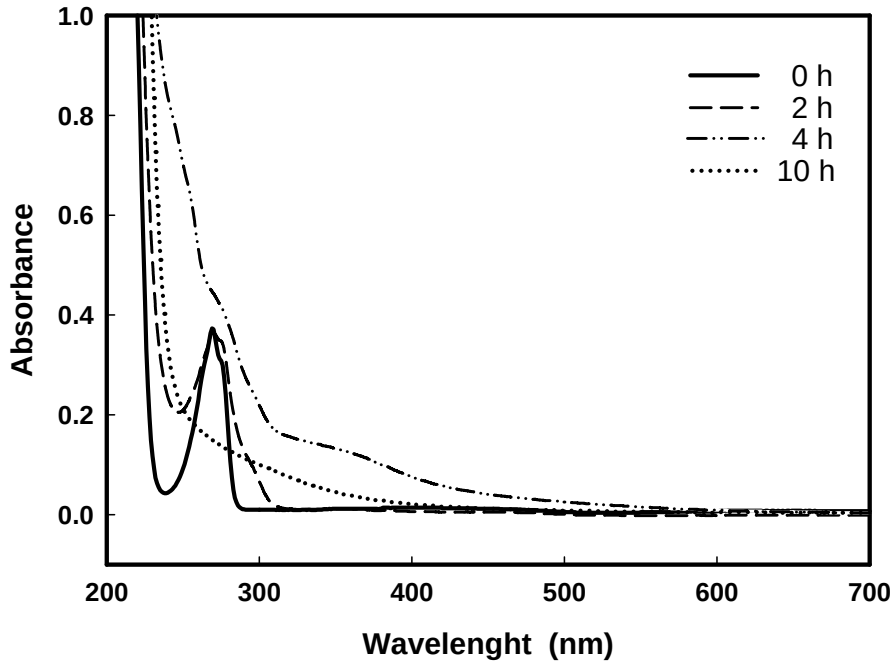


Fig. 3-2 UV-visible spectra for phenol solution degradation by ultrasonic irradiation (ultrasonic frequency, 404 kHz; intensity, 9.0 kW/m^2, initial phenol conc., 0.50 mM).

Increasing the ultrasonic intensity, the formation of intermediates with aromatic rings such as benzoquinone, catechol and hydroquinone ceased earlier as shown in Fig. 3-3,

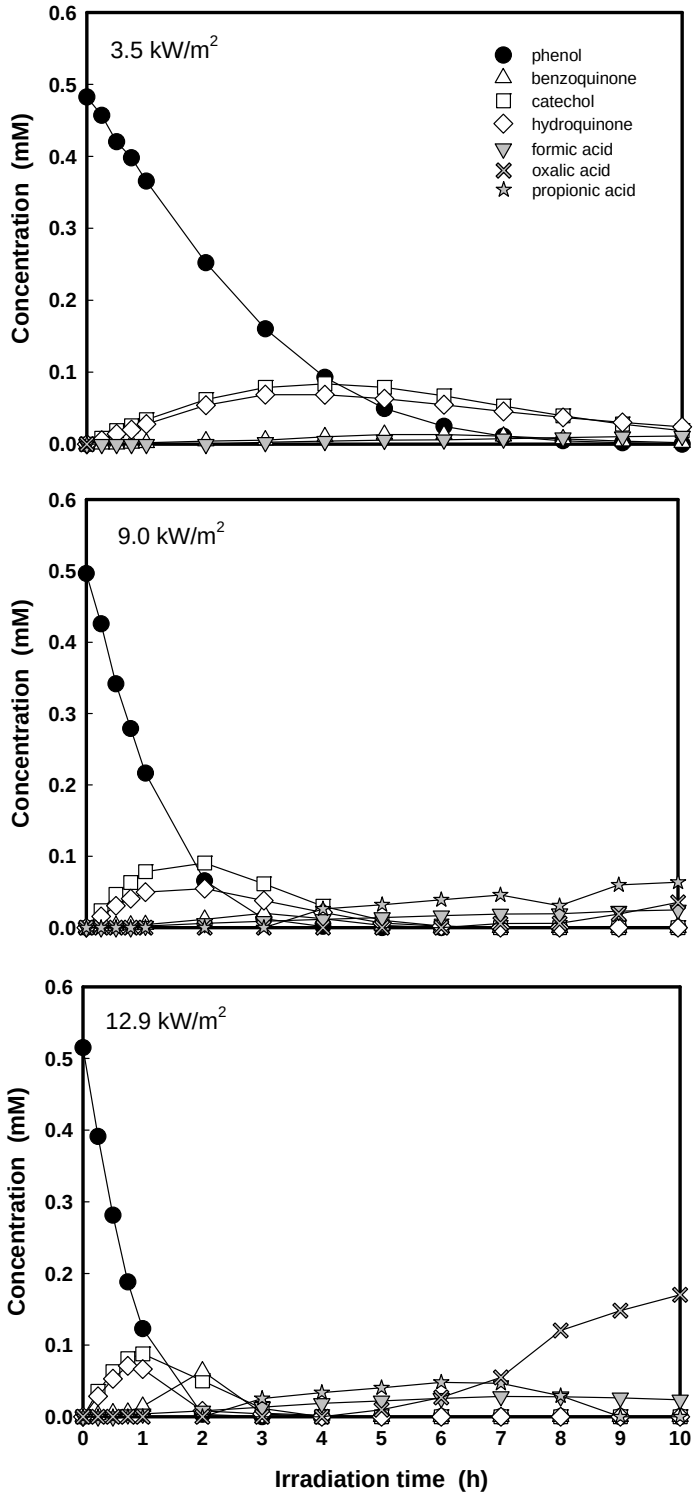


Fig. 3-3 Effect of ultrasonic intensity on phenol solution degradation, intermediates and products formation (ultrasonic frequency, 404 kHz; initial phenol conc., 0.50 mM).

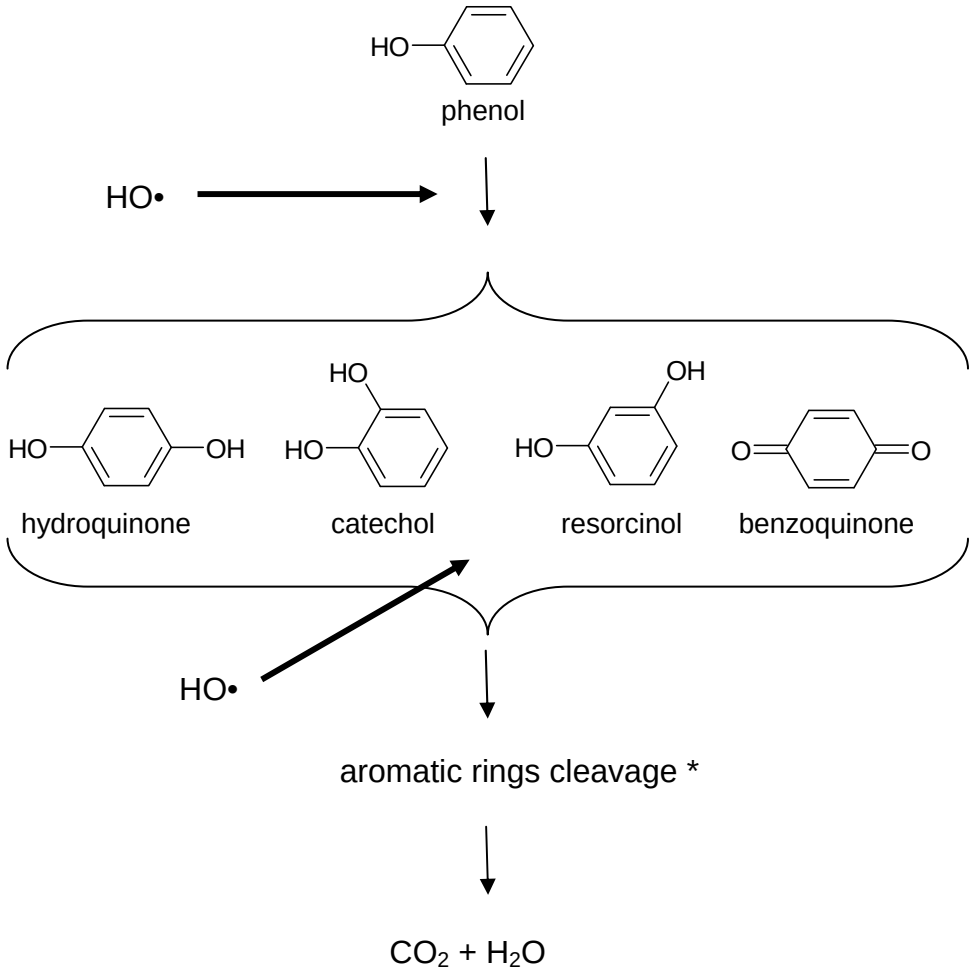
the peak of intermediates formation occurred at 4-5 h, 2 h and 1 h in the cases of 3.5, 9.0 and 12.9 kW/m^2, respectively.

At higher ultrasonic intensities, the intermediates reacted with OH radical, occasioning the cleavage of the aromatic rings and giving rise to the formation of organic acids. The concentration of low molecular weight organic acids such as formic, oxalic and propionic acid increased with an increase in the ultrasonic intensity.

Analyzing the TOC variation between the phenol solutions at 0 h and after 10 h of ultrasonic irradiation is shown in Table 3-1, the affirmation that phenol completely disappeared but part of the organic carbons remained in solution can be confirmed. The initial degradation rate constants were determined assuming pseudo first-order reaction kinetics, and increasing the ultrasonic intensity from 3.5 to 12.9 kW/m^2, increased the degradation rate by about 7 times while the TOC reduction increased about 3 times. After 10 h of ultrasonic irradiation, in the three cases, all phenol in solution disappeared but complete mineralization was not achieved. As shown in Fig. 3-3, some of the carbon atoms are still present in the form of organic acids. Fig. 3-4 shows a scheme of the phenol degradation pathway.

Table 3-1 Comparison of ultrasonic intensities regarding TOC reduction after 10 h and phenol solution initial degradation rate.

Intensity (kW/m^2)	TOC reduction (%)	k (1/s)
3.5	8.9	0.6×10^{-4}
9.0	16.7	2.2×10^{-4}
12.9	29.0	4.3×10^{-4}



* Detected organic acids after cleavage of the aromatic rings:

HOOCCOOH	CH_3CH_2COOH	HCOOH
oxalic acid	propionic acid	formic acid

Fig. 3-4 Pathway of phenol degradation by ultrasonic irradiation.

The method of hydrogen peroxide quantification by the formation of complexes utilized in this work proved to be useful and practical when traditional methods cannot be used with accuracy. It is based on Matsubara et al. [18] method, improved to be used with HPLC in place of spectrophotometer. At this case, the hydrogen peroxide-Ti-BrPAPS is determined quantitatively through a calibration curve constructed in place of analyzing the solution concentration by its inherent color as in the case of the spectrophotometer. The formation of hydrogen peroxide was examined for the three ultrasonic intensities in water and phenol solutions, as shown in Fig. 3-5.

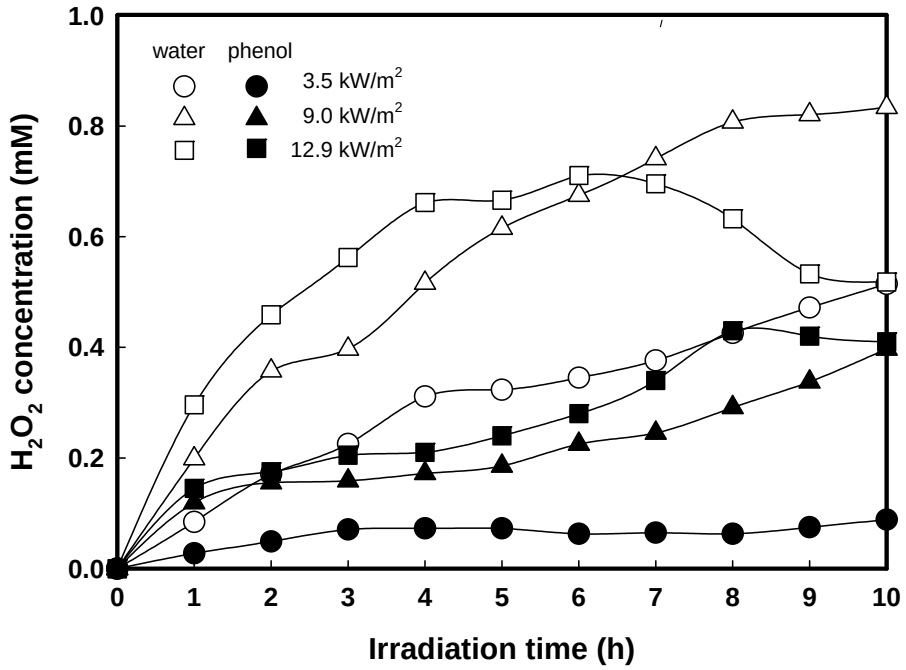


Fig. 3-5 The effect of ultrasonic intensity on hydrogen peroxide formation during water and phenol solution degradation (ultrasonic frequency, 404 kHz; initial phenol conc., 0.50 mM).

The assumption that higher ultrasonic intensities would lead to higher concentrations of hydrogen peroxide is not always valid. For water degradation, the formation of hydrogen peroxide in the case of 12.9 kW/m^2 presented a peak at 6 h (0.7 mM), and in the case of 9.0 kW/m^2, the highest concentration of hydrogen peroxide was found at 10 h (0.82 mM). Pétrier et al. [15] found that about 0.28 mM of hydrogen peroxide was

formed after irradiating ultrasounds to water in 1 h at 487 kHz and 60 W (30 kW/m^2 not calorimetrically determined), which is comparable to the present work that found 0.20 mM of hydrogen peroxide after 1 h of irradiation into water at 404 kHz and an ultrasonic intensity of 12.9 kW/m^2.

The formation of nitrous and nitric acid was also determined for the three ultrasonic intensities in both water and phenol solution systems, shown in Fig. 3-6. Nitrous acid formation was close to zero in all cases, while nitric acid formation showed an almost linear behavior within the irradiation time. High ultrasonic intensities resulted in higher concentrations of nitric acid. In the case of 12.9 kW/m^2, for example, the concentration of nitric acid after 10 h of ultrasonic irradiation reached 4.2 mM and 3.3 mM, for the water and phenol systems, respectively.

Regarding Figs. 3-5 and 3-6, there is a difference in the concentrations of H_2O_2 (Fig. 3-5) and nitric acid (Fig. 3-6) between water and phenol solutions for each ultrasonic intensity because a part of the produced radicals (for example OH radical) attacked the phenol molecules, occasioning their degradation.

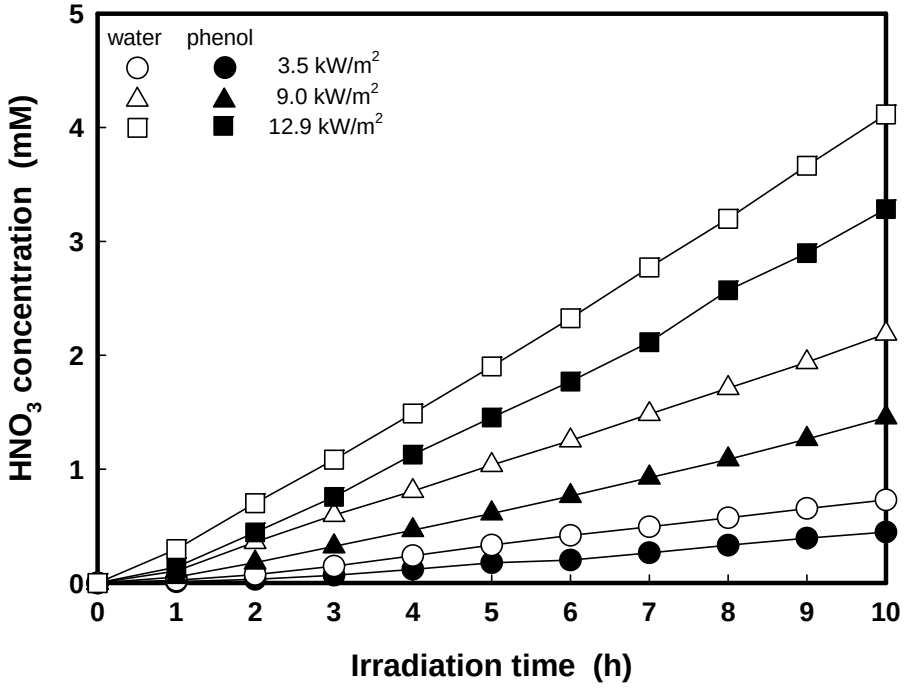


Fig. 3-6 The effect of ultrasonic intensity on nitric acid formation during water and phenol solution degradation (ultrasonic frequency, 404 kHz; initial phenol conc., 0.50 mM).

The effect of the ultrasonic intensity was also analyzed by the luminol reaction. Luminol reacts with OH radicals produced sonochemically and gives origin to aminophthalate anions and a blue fluorescence indicating the place where these reactions occur. It can be observed in Fig 3-7 that different ultrasonic intensities originate different light emissions and in the case of the ultrasonic intensity of 12.9 kW/m^2, the reactions take place in the whole reactor while in the cases of 3.5 and 9.0 kW/m^2 light is restricted to the top of the reactor (3.5 kW/m^2), and top and middle of the reactor (9.0 kW/m^2). Correlating the intensity of the light emissions to the formation of hydrogen peroxide, it can be concluded that higher light intensities are originated by higher concentrations of hydrogen peroxide.

3.3-3 Addition of $FeSO_4$ on phenol solution degradation

In order to enhance the degradability of the phenol, $FeSO_4$ was added to the solution. The Fenton like process involves a mixture of ferrous ions and hydrogen peroxide, generating radicals with a high oxidizing potential. Hydrogen peroxide utilized in the Fenton like process was ultrasonically produced during the bisphenol A degradation.

As shown in Table 3-2, a higher dosage of $FeSO_4$ did not result in higher initial rate constants. This can be explained by the fact that the concentration of hydrogen peroxide in the initial period of the reaction process was not enough to react with all iron ions released by the $FeSO_4$ and form the reactive radicals that lead to phenol destruction and in fact, hydrogen peroxide was not found in solution at any time, for any concentration of $FeSO_4$. As a result, it can be verified in Fig. 3-8 and Table 3-2, that the reduction of TOC was higher for higher amounts of Fenton's reagent. But the increase of the TOC reduction was not linear, and a steady state was achieved for $FeSO_4$ concentrations higher than 2.0 mM. In the case of high concentrations of $FeSO_4$, a precipitate, as shown in Fig. 3.9 was visually detected after 10 hours of ultrasonic irradiation. This precipitate can be $Fe(OH)_3$ as part of formed ferric ion reacted with the OH^- in solution and possibly formed ferric hydroxide.

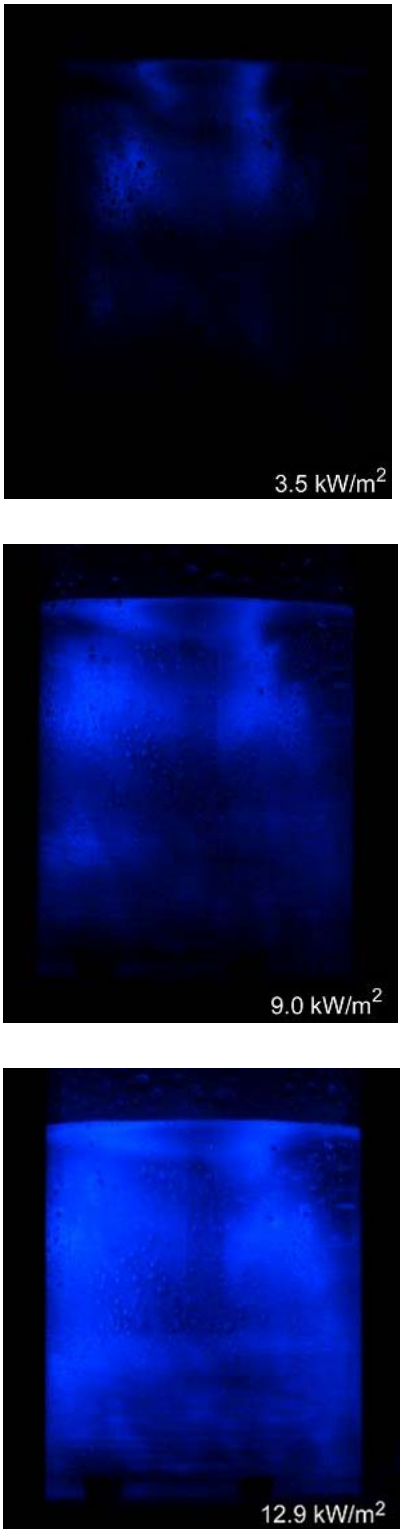


Fig. 3-7 Sonochemical-induced luminol luminescence at 3.5, 9.0 and 12.9 kW/m^2 (ultrasonic frequency: 404 kHz).

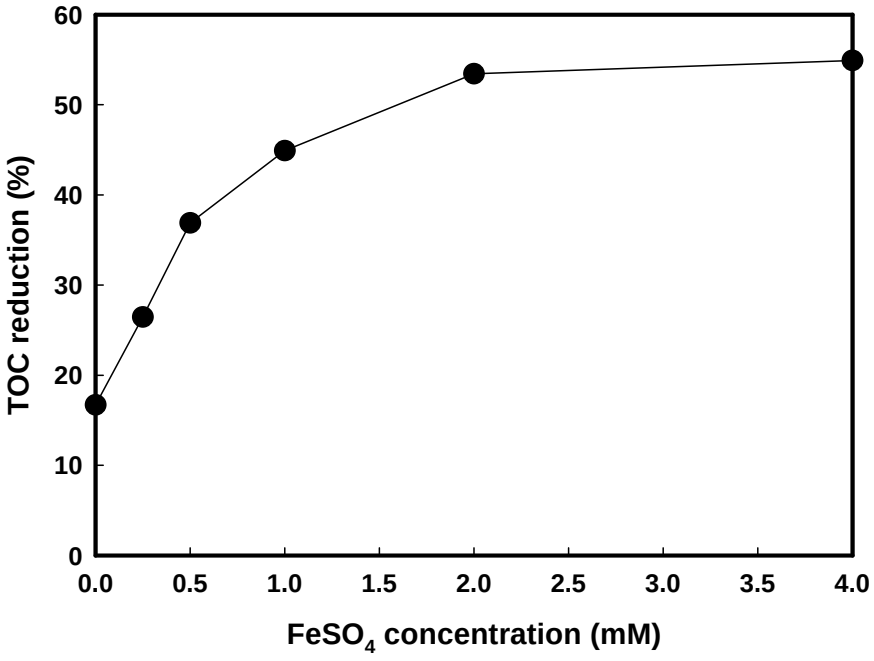


Fig. 3-8 Relationship between TOC reduction and $FeSO_4$ concentration for phenol solution degradation after 10 h of ultrasonic irradiation (ultrasonic frequency, 404 kHz; ultrasonic intensity, 9.0 kW/m^2; initial phenol conc., 0.50 mM).

Table 3-2. Comparison of $FeSO_4$ doses to TOC reduction after 10 h of ultrasonic irradiation and phenol solution initial degradation rate.

$FeSO_4$ (mM)	TOC reduction (%)	k (1/s)
0	16.7	2.2×10^{-4}
0.25	26.4	3.0×10^{-4}
0.5	36.9	3.3×10^{-4}
1.0	44.9	3.0×10^{-4}
2.0	53.4	2.9×10^{-4}
4.0	54.9	2.8×10^{-4}

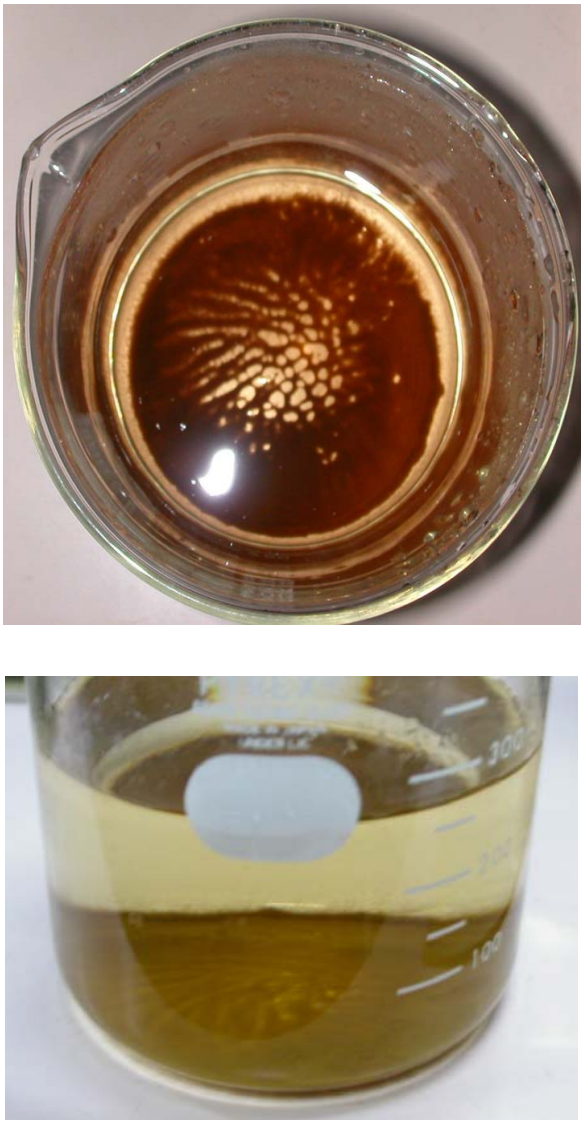


Fig. 3-9 Photograph of the precipitate formed after irradiating 0.50 mM of phenol solution for 10 h at 404 kHz and 9.0 kW/m^2, with an addition of 4.0 mM of $FeSO_4.7H_2O$.

The formation of nitrous and nitric acid for the water, phenol and phenol + 2.0 mM Fenton's reagent samples is shown in Fig. 3-10. Due to a lack of reactive radicals in the experiments in the presence of Fenton's reagent, HNO_2, which was initially formed, did not oxidize to HNO_3, and for the first six hours of ultrasonic irradiation, HNO_2 was found in higher concentration than HNO_3.

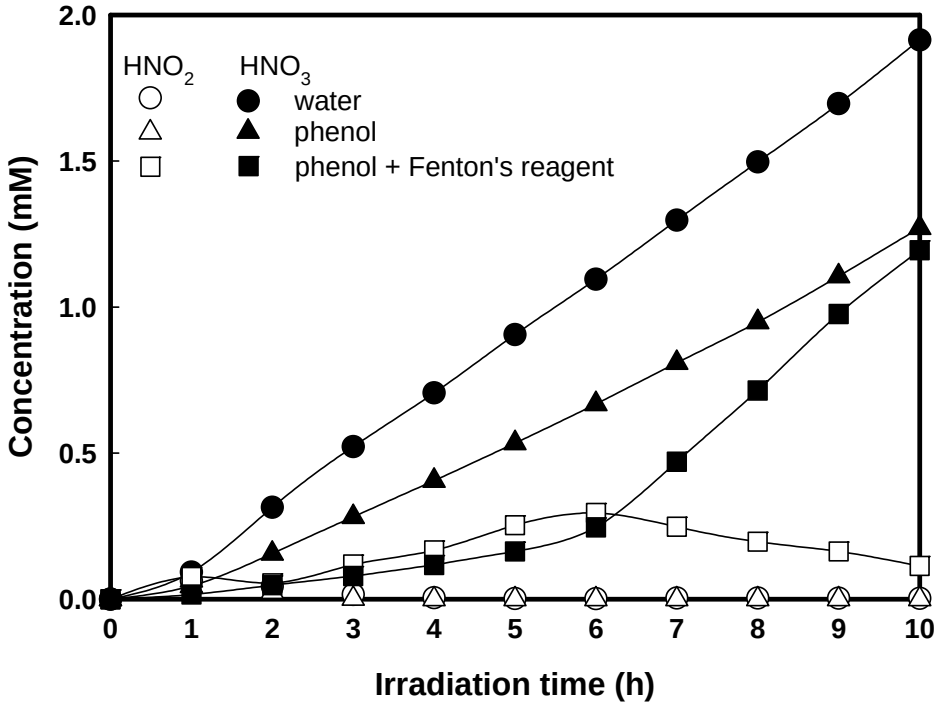


Fig. 3-10 Formation of nitrous and nitric acid during water and phenol solution degradation (ultrasonic frequency, 404 kHz; ultrasonic intensity, 9.0 kW/m^2; initial phenol conc., 0.50 mM; $FeSO_4$ conc., 2.0 mM).

Fig. 3-11 shows a comparison of phenol and intermediates concentration for systems without and with 2.0 mM of $FeSO_4$. In the presence of $FeSO_4$, some intermediates, such as benzoquinone and hydroquinone, were almost not detected in solution or showed inexpressive concentrations as mineralization proceeded. However, in this case, the cleavage of the aromatic rings may occur rapidly, and a considerable formation of organic acids was observed. Catechol was detected and showed a concentration peak after 1 h of ultrasonic irradiation but disappeared earlier than in the case without $FeSO_4$.

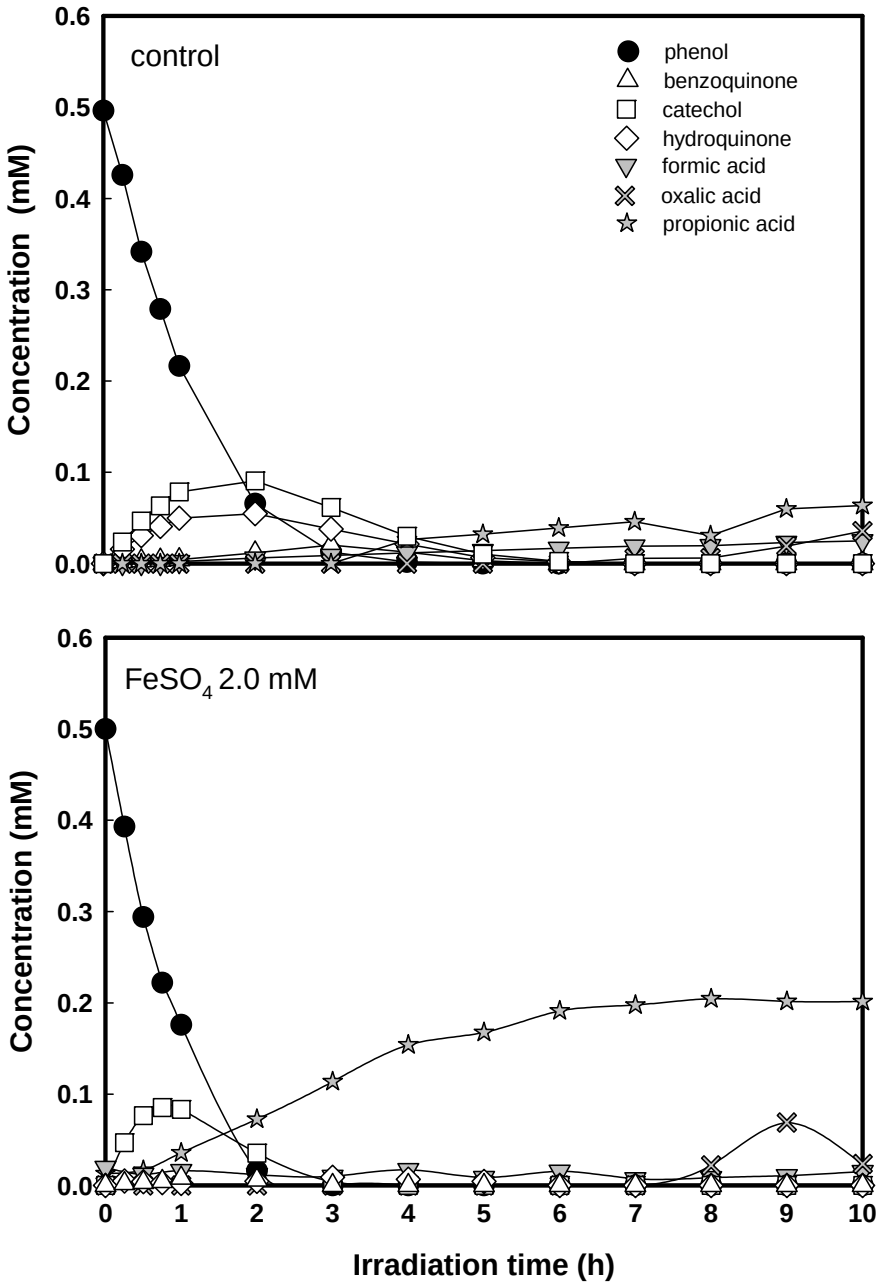


Fig. 3-11 The effect of the addition of $FeSO_4$ on phenol solution degradation (ultrasonic frequency, 404 kHz; ultrasonic intensity, 9.0 kW/m^2; initial phenol conc., 0.50 mM; $FeSO_4$ conc., 2.0 mM).

3.4 Summary

Experiments with different ultrasonic frequencies and intensities were carried out for the degradation of phenol solutions. Ultrasonic frequencies in the range of 224 to 651 presented similar data regarding to phenol degradation, and comparing ultrasonic intensities, best performance (high TOC reduction, degradation rate and concentration of nitric acid) was obtained using the highest intensity (12.9 kW/m^2), but the concentration of hydrogen peroxide did not increase linearly with an increase in the ultrasonic intensity. It was concluded that there is a straight relationship between the formations of H_2O_2, HNO_2 and HNO_3 and the phenol degradation as far as higher degradations rates were obtained when the concentrations of H_2O_2, HNO_2 and HNO_3 were higher. Gradual addition of $FeSO_4$ until a certain quantity enhanced the degradation process as well as the time to obtain a complete degradation of phenol was reduced, and the mineralization increased. Further addition of the $FeSO_4$ (more than 2.0 mM) did not increase the reduction of TOC.

3.5 References

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CHAPTER 4
Degradation of bisphenol A using sonochemical reactions

4.1 Introduction

Evidence indicates that humans, as well as domestic and wildlife species might suffer adverse consequences from exposure to chemicals that interact with endocrine system, interfering in the production, release, transport and metabolism of natural hormones [1]. One of these hazardous chemicals, bisphenol A [2, 2-bis(4-hydroxyphenyl)propane] is used in the manufacture of polycarbonate and epoxy resins, flame retardants, adhesives, paints and so on. The primary effluent in the manufacture of polycarbonates, for example, contains bisphenol A in a concentration about 100 mg/L. During the manufacturing process of these products, some bisphenol A can be inadvertently released into the environment, and thus contaminate rivers and ground waters and also can sediment and accumulate in the soil. Nowadays, there is a special interest in decontaminating the bisphenol A from polluted waters, and several processes have been developed to degrade bisphenol A. Most of the studied methods involve photocatalytic degradation [2-4] or biodegradation [5, 6]. These processes do not achieve the mineralization, and in the case of biological processes, sludge is discharged, creating another problem worse than the degradation itself.

As a new alternative to these methods, the use of sonochemical reactions has been proven to be efficient for the degradation of organic compounds in waters, as can be found in several studies regarding phenol degradation [7], dyestuffs degradation [8] and chlorinated compounds degradation [9]. However, there is a lack of research related to the use of ultrasound for bisphenol A degradation. In fact, one reference regarding the ultrasonic degradation of bisphenol A showed that the rate was accelerated by the presence of O_2 [10]. However, this work does not elucidate the degradation steps, and the detected intermediate is somewhat ambiguous.

The ultrasonic irradiation of liquids generates cavitation bubbles which grow during the compression/rarefaction cycles until they reach a critical size, and then implode generating heat and highly reactive radical species. Inside cavitation bubbles, the

temperature and pressure rise to the order of 5000 K and 100 MPa, respectively. At such conditions, water molecules degrade releasing OH and H radicals. Inside the bubble and in the liquid shell surrounding the cavity, these radicals can combine in various ways or react with the air and vapor present, leading to the detection of H_2O_2, HNO_2 and HNO_3 in the solution. These radicals can also oxidize the solute occasioning its degradation. One important advantage of the ultrasonic process is the fact that it can achieve the mineralization of the solute without producing sludge or another material that must then be discharged.

In this study, the degradation of bisphenol A in aqueous solution was carried using sonochemical reactions at different ultrasonic intensities under air atmosphere. Based on our previous work, the most effective ultrasonic frequency for the degradation of organic pollutants is around 400 kHz [8] and therefore this frequency range was used in this study. This is in agreement with Koda et al. [11] study. They found that the sonochemical effect caused by the sonolysis of water is most efficient at frequencies in the range 300-500 kHz. The relationship between bisphenol A degradation and the formation of H_2O_2 and HNO_3 was taken into account, and main intermediates of the bisphenol A degradation were identified. Furthermore, the pathways of the bisphenol A degradation by sonochemical reactions are proposed, and as the concentration of OH radicals is sufficiently high in order to be considered constant during the process, the degradation rate constants were determined assuming pseudo first-order kinetics. Experiments with the addition of different quantities of the $FeSO_4$ were also carried out in order to convert the H_2O_2 which was produced by the sonochemical reactions to radicals that then enhance the degradation process.

4.2 Materials and methods

4.2-1 Chemicals

Bisphenol A was supplied by Sigma-Aldrich Inc. USA. H_2O_2 was supplied by Sigma-Aldrich Japan, Ltd., 2-(5-bromo-2-pyridylazo)-5-[*N*-*n*-propyl-*N*- (3-sulfo propyl)amino]phenol (5-Br-PAPS), $FeSO_4 \cdot 7H_2O$, luminol, Ti and zephiramine were

purchased from Wako Pure Chemicals Industries, Ltd., Japan. Anion Mixed Standard Solution IV, utilized to calibrate the ion chromatograph, was provided by Kanto Chemical Co., Inc., Japan. All other reagents were of analytical grade commercially available.

4.2-2 Ultrasonic system

The degradation experiments were carried out in a cylindrical jacketed stainless steel reactor (ϕ 64 × 108 mm) equipped with a Langevin or piezoelectric ceramics transducer (100 – 600 kHz), made by Honda Electronics Co., Ltd., Japan. The ultrasonic power was supplied by a high frequency amplifier (L-400 BM-H, Tokyo HY-Power Lab. Inc., Japan) through a multifunction synthesizer (WF 1943, NF Electronics Instruments Co., Japan), and the temperature (25°C) was controlled by a thermostat. Vide chapter 2, Fig. 2-2 for a schematic diagram of the experimental apparatus.

4.2-3 Calorimetry

The energy dissipated by the ultrasonic apparatus was determined by calorimetry and the values of the ultrasonic intensity were cited in Chapter 2, section 2.2-3.

4.2-4 Water and bisphenol A solution degradation under ultrasonic irradiation

Air-saturated water (250 mL) was irradiated using ultrasound with a frequency of 404 kHz and ultrasonic intensities of 3.5, 9.0 and 12.9 kW/m^2 for 10 h. Samples were taken at every hour to measure the pH and the concentrations of H_2O_2, HNO_2 and HNO_3.

Bisphenol A solutions (0.50 mM, 250 mL) were prepared using air-saturated water and irradiated with ultrasound for 10 h at the same ultrasonic conditions cited above. Samples were taken at every hour to measure the pH and concentrations of bisphenol A, H_2O_2, HNO_2, HNO_3, formaldehyde and organic acids. The total organic carbon (TOC) was evaluated for the solutions at 0 and 10 h, and UV-visible spectra were also evaluated for every sample. Additional samples were taken at 15, 30 and 45 min in order to determine the kinetics of the reactions.

The effect of $FeSO_4$ addition in order to promote Fenton like reactions was evaluated for solutions with the concentrations of 0.25, 0.50, 1.0, 2.0 and 4.0 mM of $FeSO_4$ at 404 kHz of ultrasonic frequency and 9.0 kW/m^2 of ultrasonic intensity. The source of H_2O_2 that reacts in Fenton like reactions is the combination of the ultrasonically produced radicals during the bisphenol A degradation process.

4.2-5 Analytical procedures

In order to determine the intermediates of the bisphenol A degradation, samples were taken after 1 h of reaction, extracted with ethyl acetate and concentrated using an evaporator. Qualitative analysis was made using a GC/MS analyzer (GC-MS QP5000, Shimadzu Corp., Japan) equipped with a VF-5ms capillary column (30 m × 0.25 mm i. d., Varian, Inc., USA) in helium carrier gas; and the oven temperature was held at 80 °C for the first 2 min, then raised at a rate of 5 °C/min up to 230 °C and held at 230 °C for 20 min.

Quantitative analysis of bisphenol A was carried out using HPLC with a UV-visible detector (8020 series, Tosoh Corp., Japan) and a reverse phase column ODS-100S (Tosoh Corp., Japan) under the conditions as follows: wavelength, 270 nm; column temperature, 40 °C; mobile phase, 0.1 % phosphoric acid 55 % + methanol 45 % (vol); flow rate, 1.0 mL/min. Concentrations of H_2O_2 were obtained as follows: samples were reacted with Ti-5-Br-PAPS for 75 min at 40 °C, and the produced complex was analyzed by HPLC with a UV-visible detector (8020 series, Tosoh Corp., Japan) and a reverse phase column Mightysil RP-18 GP (Kanto Chemical Co., Inc., Japan) under the conditions as follows: wavelength, 535 nm; column temperature, 40 °C; mobile phase, acetonitrile 33 %+ 0.25 M sodium acetate 2 %+ 1.0 mM zephiramine 2% + distilled water 63% (wt); flow rate, 1.0 mL/min. Concentrations of HNO_2, HNO_3 and organic acids were determined using the ion chromatograph with an electroconductivity detector (10A series, Shimadzu Corp., Japan) and an ion exchange column under the conditions as follows: column type, IC-A3; column temperature, 40 °C; mobile phase, 16.0 mM *p*-hydroxybenzoic acid 50% + 6.4 mM Bis-Tris 50% (wt); flow rate, 1.0 mL/min. Concentration of formaldehyde was analyzed using the Formaldehyde-Test supplied by

Wako Pure Chemical Industries Ltd., Japan. The UV-visible spectrum was obtained by a spectrophotometer (U-3200, Hitachi, Ltd., Japan). The TOC analysis was performed using a TOC analyzer (TOC-5000A, Shimadzu Corp., Japan).

4.3 Results and discussion

4.3-1 Effect of ultrasonic intensity on bisphenol A solution degradation

Keeping the ultrasonic frequency constant (404 kHz), experiments were carried out at intensities of 3.5, 9.0 and 12.9 kW/m^2. Fig. 4-1 shows the decrease of bisphenol A concentration under the three different intensities. Bisphenol A degraded completely after 10, 3 and 2 h of ultrasonic irradiation, respectively, showing that an increase in the ultrasonic intensity also induces an increase in the degradation rate. During the HPLC analysis, besides the bisphenol A peak, a strong peak was detected, and a posterior GC/MS analysis indicated that this substance was possibly 2-(3,4-dihydroxyphenyl)-2-(4-hydroxyphenyl)propane, commonly known as 3-hydroxybisphenol A. Due to a lack of this substance in the standard, its quantity was only estimated by its relative area in the chromatogram. It can be observed in Fig. 4-1 that in the first 3 h of reaction, 3-hydroxybisphenol A levels increase as long as bisphenol A decreases, this is understandable since the first step of the bisphenol A degradation would result mainly from the addition of OH radical to the bisphenol A aromatic ring. As the intermediate 3-hydroxybisphenol A is then attacked by other radicals, it degrades giving rise to other substances. By increasing the ultrasonic intensity, the consumption rate of 3-hydroxybisphenol A increased, indicating that it is related to the quantity of radicals available in solution. The occurrence of thermal degradation was also verified with the addition of a radical scavenger to the bisphenol A solution. An addition of 25 mM t-butyl alcohol inhibited largely the degradation rate. This indicates that the bisphenol A degradation occurs mainly by reaction with free radicals rather than pyrolysis.

The degradation rate constants obtained from the data within the first hour of ultrasonic irradiation were 0.84, 2.48 and 4.50 $\times$ 10^{-4} (1/s) for the ultrasonic intensities of 3.0, 9.0 and 12.9 kW/m^2, respectively; as expected, higher degradation rates were

obtained by higher ultrasonic intensities.

The TOC reduction degree between the bisphenol A solutions at 0 h and after 10 h of ultrasonic irradiation were 12.4, 15.4 and 20.2 % at the ultrasonic intensities of 3.0, 9.0 and 12.9 kW/m^2, respectively. As the ultrasonic intensity increased, the quantity of radicals present in the bisphenol A solution also increased, and as a consequence, the TOC reduction also increased. At the three different ultrasonic intensities, although bisphenol A completely disappeared, complete mineralization was not achieved; most of the organic carbons remained in solution in the form of organic compounds with low molecular weight such as organic acids.

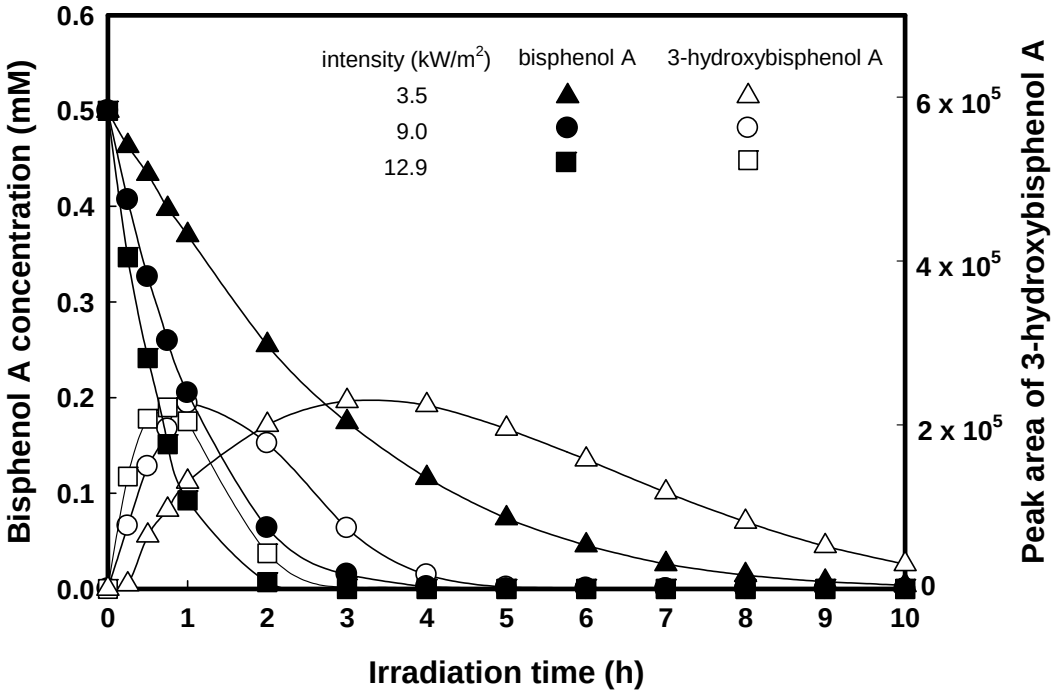

Fig. 4-1 Influence of the ultrasonic intensity on bisphenol A solution degradation and formation of the intermediate 3-hydroxybisphenol A (ultrasonic frequency: 404 kHz).

4.3-2 Formation of H_2O_2 and HNO_3 during water and bisphenol A solution degradation.

The method of H_2O_2 quantification by the formation of complexes utilized in this work proved to be useful and practical when traditional methods cannot offer accuracy or precision. Based on the method of Matsubara et al. [12] it is improved by using a HPLC in place of the spectrophotometer. In this case, the complex H_2O_2-Ti-BrPAPS is determined quantitatively through a calibration curve constructed in place of analyzing the solution concentration by its inherent color as in the case of the spectrophotometer.

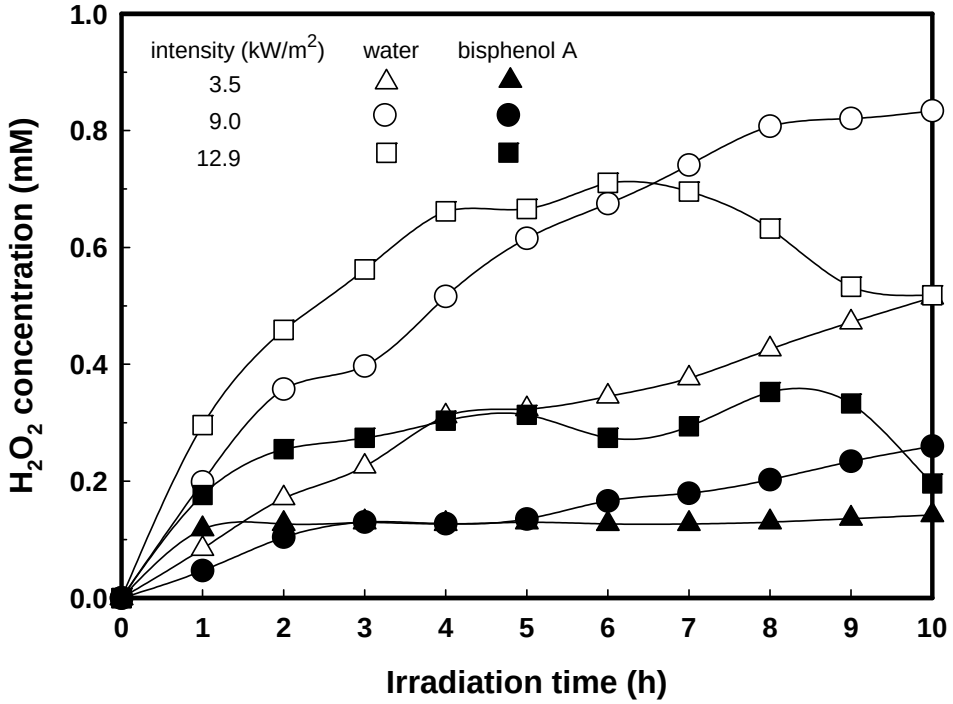

Fig. 4-2 Influence of ultrasonic intensity on H_2O_2 formation during water and bisphenol A solution degradation (ultrasonic frequency: 404 kHz).

The formation of H_2O_2 was examined for the three ultrasonic intensities in water and bisphenol A solution systems, as shown in Fig. 4-2. The assumption that higher ultrasonic intensities would lead to higher concentrations of H_2O_2 is not always valid. One of the reasons for this is suggested from the fact that the formation of HNO_3 is almost linear and the reaction to form it from HNO_2 acid consumes H_2O_2 itself or a part

of the radicals which would recombine forming H_2O_2. Also, at high ultrasonic intensities, H_2O_2 may react with OH radicals and form less reactive species like HOO radicals. For water degradation, the formation of H_2O_2 in the case with an intensity of 12.9 kW/m^2 presented a peak at 6 h (0.7 mM), and in the case of 9.0 kW/m^2, the highest concentration of H_2O_2 was found at 10 h (0.82 mM) Pétrier et al. [13] found that about 0.28 mM of H_2O_2 was formed after ultrasonically irradiating water for 1 h at 487 kHz and 60 W (30 kW/m^2 not calorimetrically determined). This is comparable to the present work that found 0.20 mM of H_2O_2 formed from water after 1 h of irradiation at 404 kHz and an ultrasonic intensity of 12.9 kW/m^2.

In case of bisphenol A degradation, the quantity of H_2O_2 produced in each intensity was lower compared to that of each respective water sample.

The formation of HNO_2 and HNO_3 was also determined for the three ultrasonic intensities in both water and bisphenol A solution systems, as shown in Fig. 4-3. The mechanism of HNO_2 and HNO_3 formation in the reaction of the ultrasonically produced radicals under air atmosphere is shown in our previous work [8].

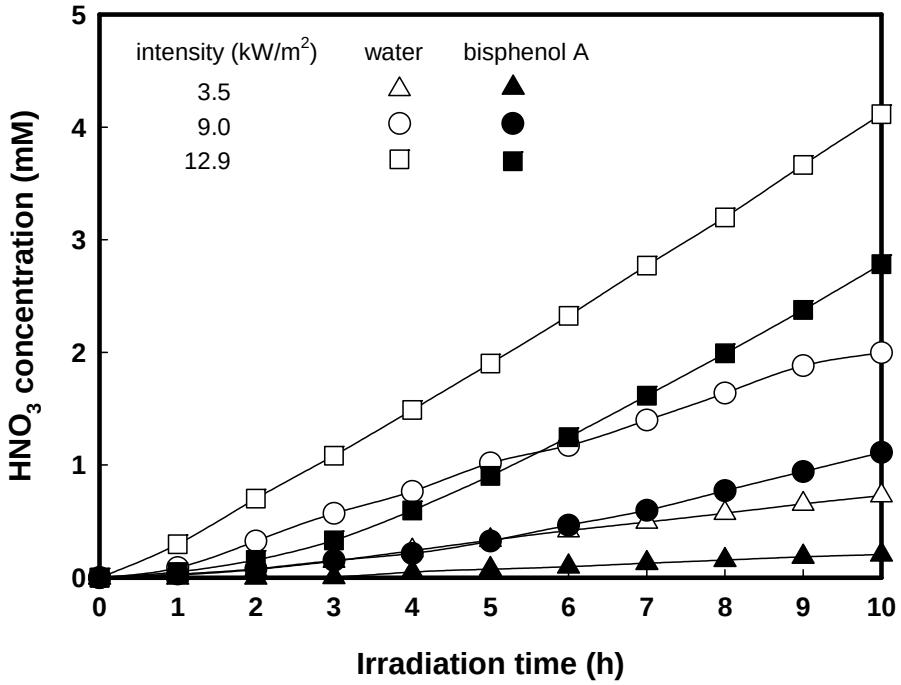

Fig. 4-3 Influence of ultrasonic intensity on HNO_3 formation during water and bisphenol A solution degradation (ultrasonic frequency: 404 kHz).

HNO_2 concentration was close to zero in all cases because it was converted to nitric acid, as explained before. HNO_3 formation showed an almost linear behavior within the irradiation time. High ultrasonic intensities resulted in higher concentrations of HNO_3. In case of 12.9 kW/m^2, for example, the concentration of HNO_3 after 10 h of ultrasonic irradiation reached 4.2 mM and 3.0 mM, for the water and bisphenol A systems, respectively. After 10 h of ultrasonic irradiation, pH values were around 3.0 for all cases. Regarding Figs. 4-2 and 4-3, there is a difference in the concentrations of H_2O_2 (Fig. 4-2) and HNO_3 (Fig. 4-3) between water and bisphenol A solution for each ultrasonic intensity because some of the radicals produced (for example OH radical) attacked the bisphenol molecules, occasioning their degradation, and consequently, less radicals were available to produce H_2O_2 and HNO_3.

4.3-3 Formation of intermediates during bisphenol A solution degradation.

Fig. 4-4 shows the UV-visible spectra for 0-10 h of bisphenol A solution degradation at 404 kHz and 9.0 kW/m^2.

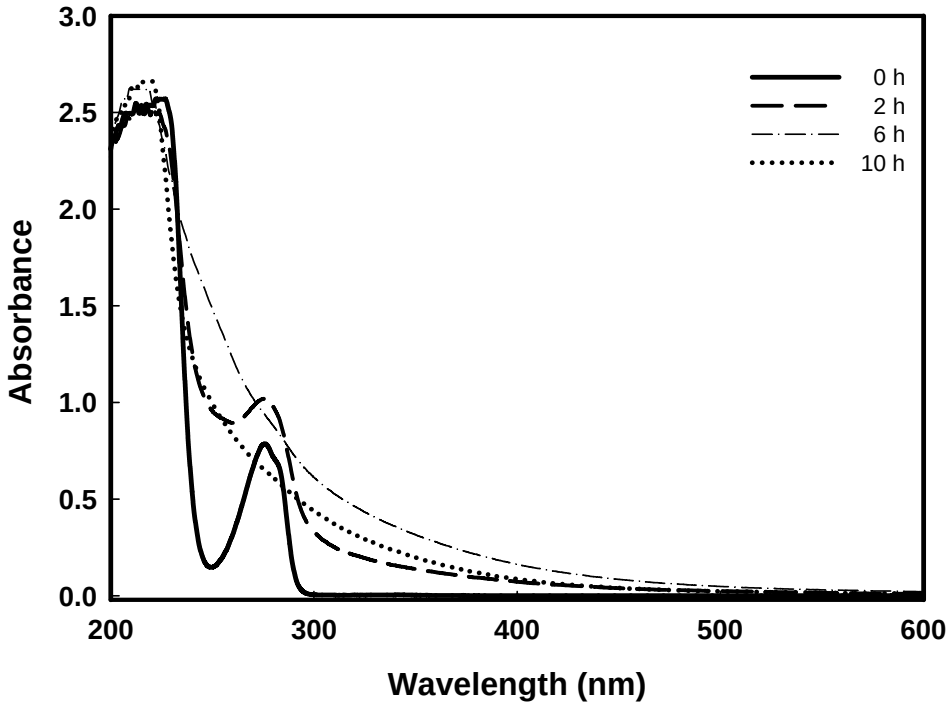

Fig. 4-4 UV-visible spectra for bisphenol A solution degradation by ultrasonic irradiation (ultrasonic frequency: 404 kHz, ultrasonic intensity: 9.0 kW/m^2).

An increase in the peak height is observed around 270 nm after 2 h of reaction, indicating the formation of intermediates with aromatic rings. As the irradiation time increases, the peaks decrease, indicating the occurrence of the aromatic rings cleavage. After 10 h, the peaks of the aromatic rings decreased considerably but not completely, indicating that organic substances are still present in solution.

Fig. 4-5 (a, b, c) shows the data obtained by the GC/MS analyzer. Comparing it with the Wiley Library and standard chromatograms of organic substances, it was found that at one hour of ultrasonic irradiation, benzoquinone, phenol, catechol, hydroquinone, 2-(4-hydroxyphenol)-2-propanol and 4-hydroxyacetophenone were present in solution as intermediates but in very low concentration. 3-Hydroxybisphenol A, as explained in section *4.3-1*, was the main intermediate found in the bisphenol A degradation process. Imai et al. [14], who studied the removal of bisphenol A using microorganisms, also found this compound as a degradation product. In addition, their EI-MS spectrum was essentially identical to the one obtained in the current study as shown in Fig. 4-5 (b).Furthermore, 4-(1-methylethenyl)phenol (Fig. 4-5 (c)) was detected and identified by comparison with the MS spectrum obtained by Fukuda et al. [15].

Fig. 4-6 shows the proposed pathways for the bisphenol A solution degradation. The bisphenol A degradation was assumed to have three different paths (I – III). Path I: OH radical reacts with bisphenol A to form 3-hydroxybisphenol A which was the main intermediate found in this study, and after the loss of a proton, catechol and compound (A) are formed. Path II: addition of a proton to bisphenol A to form compound (A) and phenol. Compound (A) reacts with water and produces 2-(4-hydroxyphenyl)-2-propanol or 4-(1-methylethenyl)phenol, upon the loss of a proton, which could react with OH radical and produce (C). Compound (C) can react with further OH radical or H_2O_2 producing 4-hydroxyacetophenone. In path III, bisphenol A reacts with 2 mole equivalent of OH radicals to form compound (B), which can form (A) or hydroquinone. Hydroquinone can be oxidized to form benzoquinone. Continuous reaction with radicals will induce the aromatic ring cleavage, forming light weight hydrocarbons such as formaldehyde, formic and propionic acids.

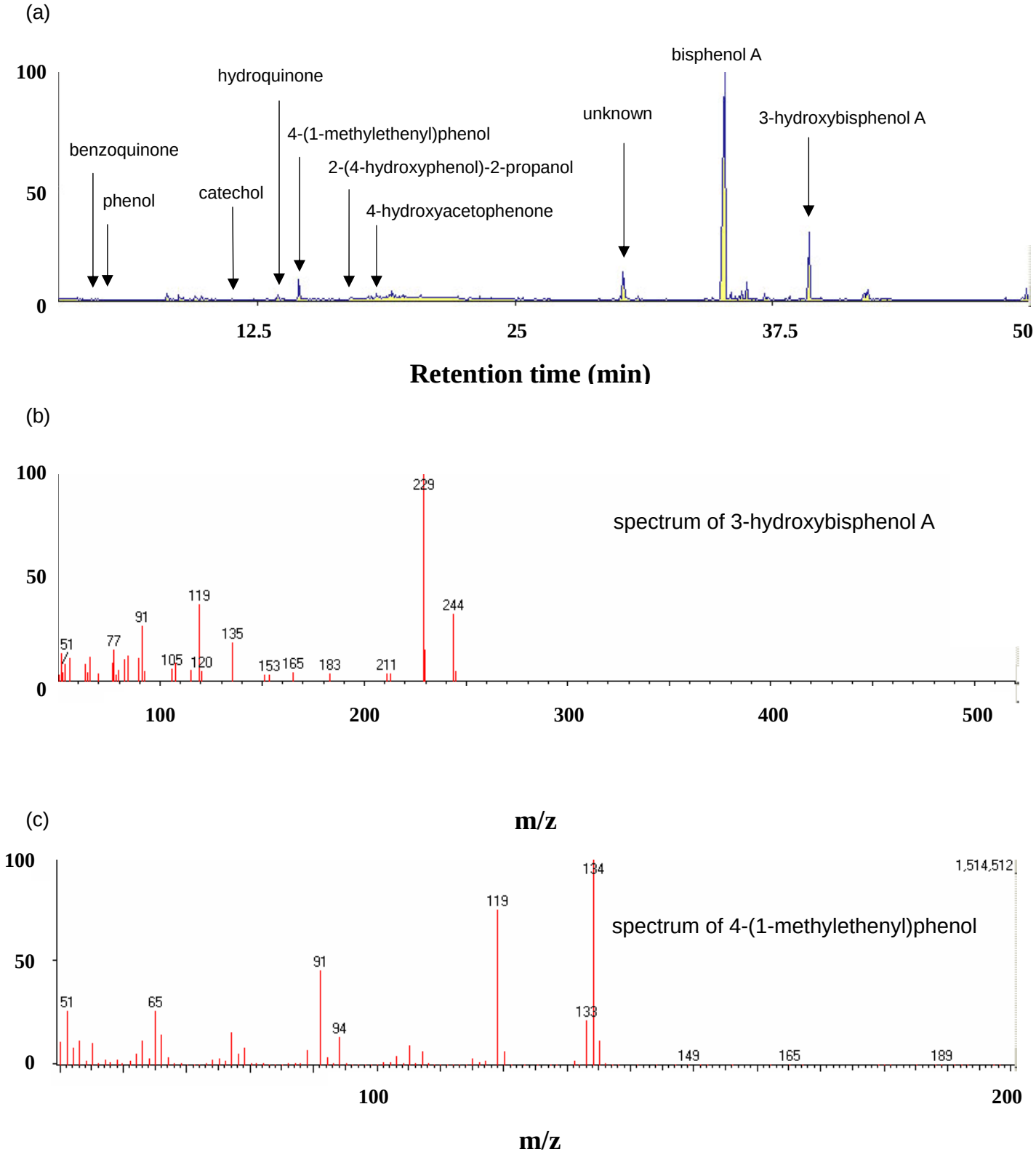

Fig. 4-5 GC/MS chromatogram of bisphenol A solution, 4-hydroxybisphenol A and 4-(1-methylethenyl)phenol spectra after one hour of ultrasonic irradiation at 404 kHz and 9.0 kW/m^2.

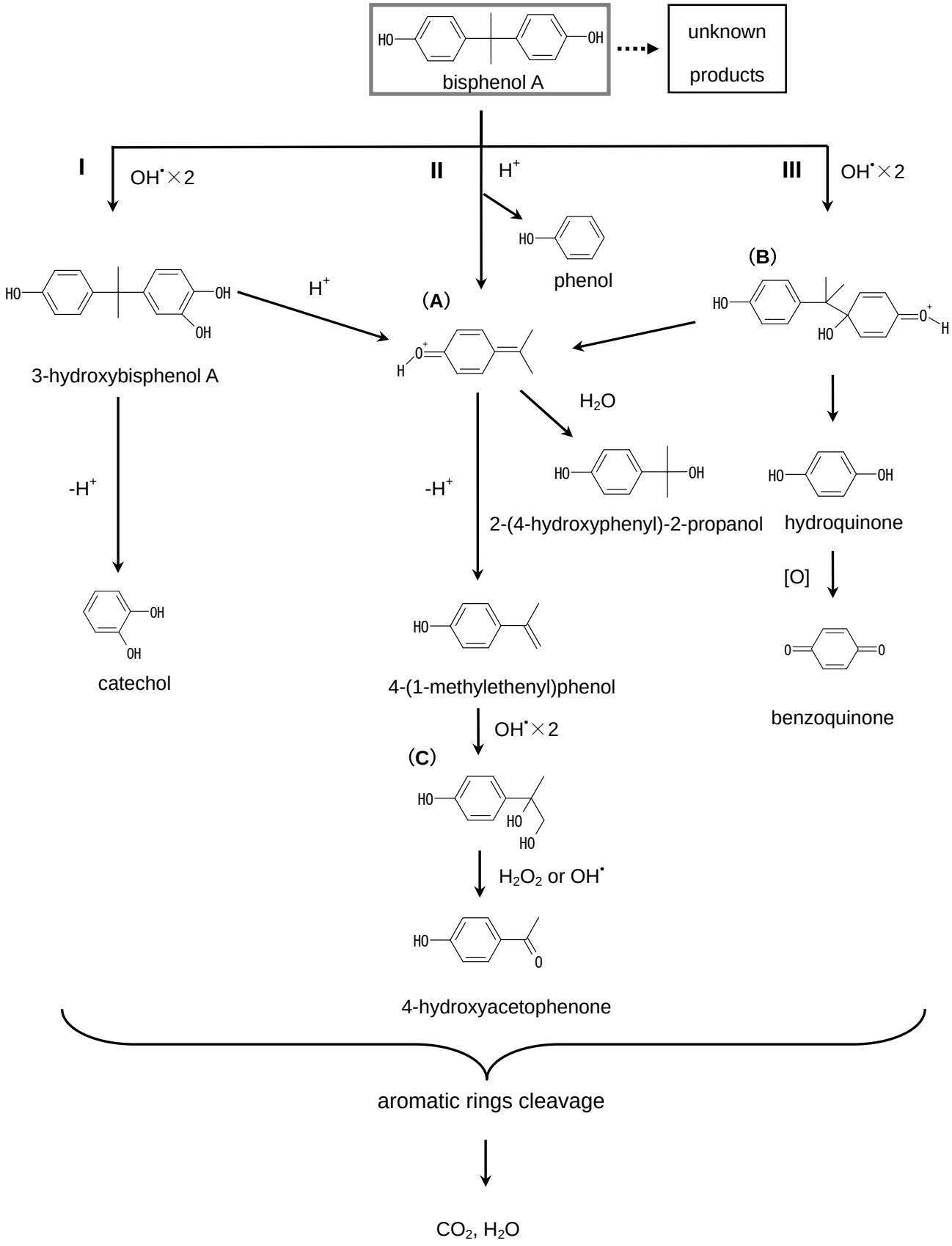

Fig. 4-6 Proposed pathways of bisphenol A solution degradation by ultrasonic irradiation.

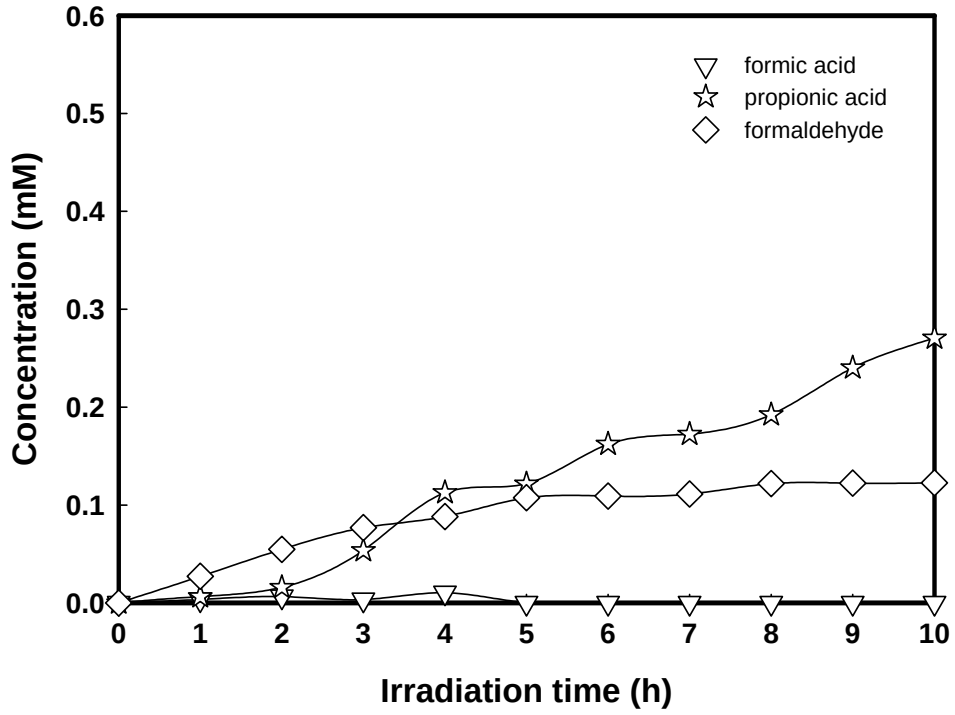

Fig. 4-7 Formation of organic acids and formaldehyde during bisphenol A solution degradation at 404 kHz and 9.0 kW/m^2.

Fig. 4-7 shows the concentrations of formaldehyde, formic acid and propionic acids detected. Mineralization of the solution gives rise to the formation of CO_2 and H_2O.

4.3-4 Addition of $FeSO_4$ on bisphenol A solution degradation

Some efforts to improve the efficiency of the sonochemical reactions increase the formation of OH radicals, facilitating the degradation. One of these efforts is the addition of $FeSO_4$, which enhances the amount of OH radicals available in solution. The formation of $OH^{\bullet}$ can be expressed by the equation (4-1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \qquad (4\text{-}1)$$

The radicals generated in the Fenton like process have an oxidizing potential of 2.8 V vs. NHE (normal hydrogen electrode) and are capable of oxidizing wide range of

organic compounds found in wastewaters [16]. Further increases in the concentration of Fe^{2+} showed no further catalytic activity, due to the direct reduction of OH radicals by the metal ions, as shown by the equation (4-2):

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^{-} \qquad (4\text{-}2)$$

As shown in Fig. 4-8, the addition of $FeSO_4$ only slightly increased the degradation. This can be explained by the fact that the concentration of H_2O_2 in the initial period of the reaction process was not enough to react with all iron ions released by Fenton like reactions and form the reactive radicals that lead to bisphenol A destruction. Furthermore, H_2O_2 was not found in solution at any time for any concentration of $FeSO_4$. As a result, it can be verified in Table 4-1 that the reduction of TOC was higher for higher amounts of $FeSO_4$. But the increase of the TOC reduction was not linear, and for $FeSO_4$ concentrations higher than 2.0 mM, the solution became saturated and as the formation of H_2O_2 was limited, no additional conversion to OH radical occurred. During the degradation process catalyzed by the $FeSO_4$, a precipitate was visually detected. This precipitate may be $Fe(OH)_3$ as some of the ferric ions may have reacted with the OH^- in solution, as shown by equation (4-2). The pH found after 10 h of reaction was around 3.0 for every quantity of $FeSO_4$.

The effect of the addition of 2.0 mM $FeSO_4$ on TOC reduction was also analyzed for the ultrasonic intensities of 3.5 and 12.9 kW/m^2. The difference in the TOC reduction between the solutions with and without $FeSO_4$ at the same intensity was similar to that found for 9.0 kW/m^2.

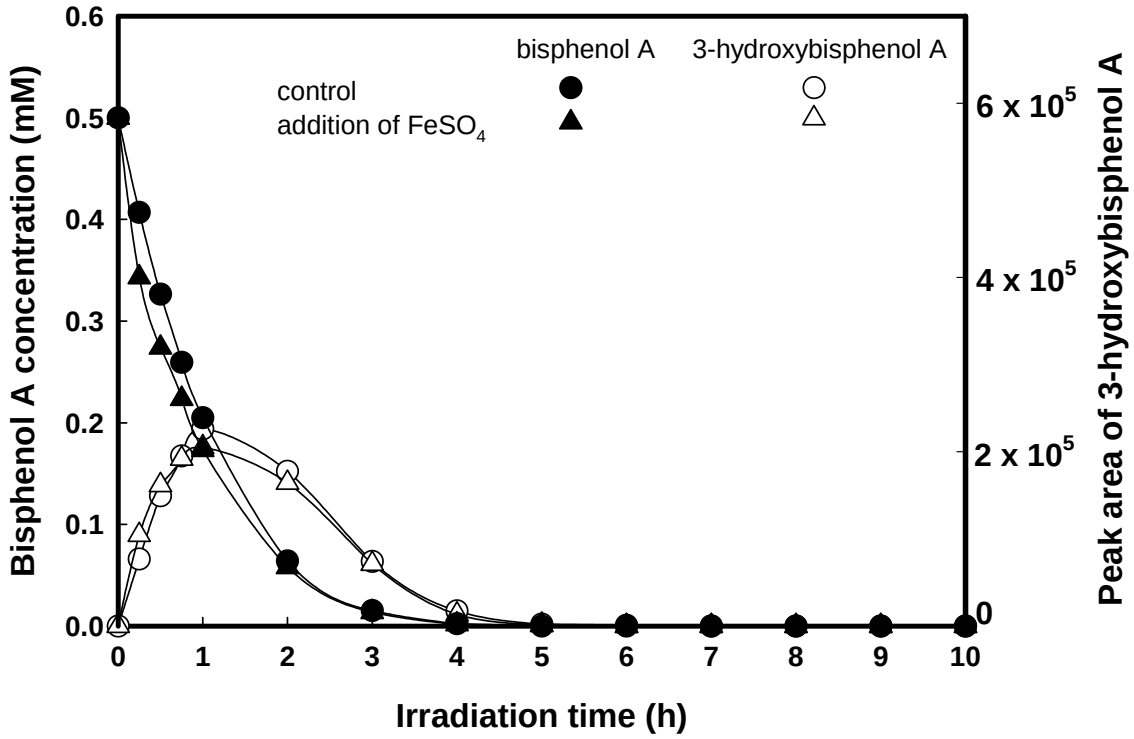

Fig. 4-8 Degradation of bisphenol A solution and formation of 3-hydroxybisphenol A in systems with and without addition of 2.0 mM of $FeSO_4$ at 404 kHz and 9.0 kW/m^2.

Table 4-1 Variation of TOC between 0 and 10 h of ultrasonic irradiation for different quantities of the $FeSO_4$ at 404 kHz and 9.0 kW/m^2.

$FeSO_4$ (mM)	TOC reduction (%)
Control	15.4
0.25	25.6
0.5	29.6
1.0	41.5
2.0	47.8
4.0	50.2

4.4 Summary

Experiments with different ultrasonic intensities were carried out to determine the efficiency degradation of bisphenol A in solution. High intensities generated the best TOC reductions and a faster degradation of bisphenol A. It was concluded that there is a close relationship between the formations of H_2O_2, HNO_2 and HNO_3, and the bisphenol A degradation. For example, when water is ultrasonically irradiated, larger amounts of H_2O_2 and HNO_3 are formed, while when bisphenol A is irradiated, some of the radicals that would form these compounds are instead used in the steps to degrade the bisphenol A. However, low concentrations of H_2O_2 and HNO_3 are still found in solution. Intermediates of the bisphenol A degradation were identified and probable degradation pathways were proposed based on the sonochemical reactions and the radicals produced. After 10 h of ultrasonic irradiation, the bisphenol A degradation products obtained were formic acid, propionic acid and formaldehyde. Gradual addition of $FeSO_4$ did not reduce the time necessary to degrade bisphenol A but increased significantly the degree of the mineralization.

4.5 References

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CHAPTER 5
General conclusion

The author investigated the use of ultrasonic waves to degrade solutions of organic pollutants such as dyestuffs, phenol and bisphenol A. Parameters like ultrasonic frequency and intensity were evaluated, and the degradation effectiveness was correlated to the presence of H_2O_2 in solution.

In Chapter 2, the degradation of water at frequencies in the range 100 – 700 kHz and ultrasonic intensity of 9.0 kW/m^2 was investigated. Regarding the time course of hydrogen peroxide and nitric acid formation, the frequencies in the range 200 – 700 kHz presented similar behavior. The frequency of 118 kHz showed low values for both hydrogen peroxide and nitric acid formations. For the degradation of dyestuffs, best results were obtained by the ultrasonic frequency of 404 kHz. Keeping the frequency constant at 404 kHz, higher degradation rates were obtained using the ultrasonic intensity of 12.9 kW/m^2. In the best conditions, Rhodamine B and Orange II solutions became colorless after 2 and 4 h of ultrasonic irradiation, respectively.

Chapter 3 described the development of a system to degrade phenolic compounds using sonochemical reactions. Several ultrasonic frequencies and input powers were tested in order to optimize the degradation of phenol solutions. The formation of unstable intermediates during the degradation process such as benzoquinone, catechol and hydroquinone was also analyzed. Organic acids were recognized as the final products. Furthermore, the importance of the formations of hydrogen peroxide, nitric and nitrous acid caused by ultrasonic cavitation was taken into account. The variation of pH and total organic carbon values (TOC) were also investigated. At the optimal ultrasonic frequency, phenol disappeared after 4 h of ultrasonic irradiation (phenol initial conc., 0.50 mM; ultrasonic frequency, 404 kHz; ultrasonic intensity, 9.0 kW/m^2). In order to improve degradation, experiments in the presence of $FeSO_4$ were carried out, and an increase of 50 % in the reaction rate was obtained with the addition of 0.50 mM of $FeSO_4$.

Chapter 4 showed the sonochemical degradation of bisphenol A in aqueous solution.

Bisphenol A is a suspected endocrine disruptor, which can cause several damages for humans, animals and the environment. Experiments were done at different ultrasonic intensities under air atmosphere. Bisphenol A (0.50 mM) was completely degraded after 10, 3 and 2 h of ultrasonic irradiation at a frequency of 404 kHz, and intensity of 3.5, 9.0 and 12.9 kW/m^2, respectively. During ultrasonic irradiation, some aromatic intermediates, such as 2-(4-hydroxyphenyl)-2-(3,4-dihydroxyphenyl)propane, commonly known as 3-hydroxy -bisphenol A were detected. Further cleavage of the aromatic rings resulted in other products, like formaldehyde and organic acids were also being detected. The proposed pathways of bisphenol A degradation by ultrasonic irradiation are based on the above mentioned intermediates. The relationship between bisphenol A degradation and formation of hydrogen peroxide and nitric acid was taken into account, correlating this to the radicals that take part in the degradation process. In order to optimize the performance of the ultrasonic system, additional experiments with $FeSO_4$ were also carried out. However the addition of $FeSO_4$ did not increase bisphenol A degradation rates. Compared to the system without $FeSO_4$, the total organic carbon concentration (TOC) was reduced by about 30 %, at 404 kHz and 9.0 kW/m^2.

5.1 The future use of sonochemistry for environmental protection

Ultrasounds has proven to be a useful tool for the degradation of organic compounds in wastewater, although complete mineralization cannot be achieved in some cases. Studies focusing the combination of ultrasounds with other methods (for example, photocatalysis, enzyme treatment) must be made in order to optimize the total degradation process and also experiments aiming a rescale for practical uses are also necessary. Probably in a near future the benefits of sonochemistry will be commodiously applied for the welfare of mankind.

List of publications

(1) Marcio Inoue, Fumio Okada, Akihiko Sakurai, Mikio Sakakibara:
A new development of dyestuffs degradation system using ultrasound,
Ultrasonics Sonochemistry, **13** (2006) 313-320.

(2) M. Inoue, T. Kimura, F. Okada, A. Sakurai, M. Sakakibara:
Degradation of hazardous phenols using sonochemical reactions,
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Acknowledgements

The studies presented in this thesis were carried out at the Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, University of Fukui from 2003 to 2008 under the guidance of Professor Mikio Sakakibara. The author wishes to express his sincere gratitude to Professor Mikio Sakakibara for his constant guidance, valuable discussion and patience throughout this work.

The author wishes to thank Associate Professor Akihiko Sakurai for his invaluable guidance and discussion.

The author is grateful to Mr. Fumio Okada for his important technical support.

The author wishes to thank Professor Hiroyuki Uchida, Associate Professor Jun'ichiro Miura and Associate Professor Ichiro Takahashi for their discussion and comments.

The author also thanks all other teachers of the Department of Applied Chemistry and Biotechnology for their support.

The author would like to acknowledge the Japanese Government Scholarship from the Ministry of Education, Culture, Sports, Science and Technology.

The author is grateful to the personnel of the International Students Affairs and the teachers of the International Student Center, for their kindness and support.

The author wishes to thank Professor Fujio Yamamoto, Professor Kiyoshi Nakashima, Dr. Eckhard Hitzer, Dr. Mary Becker and Ms. Toshimi Zen for their kind help and support.

The author is thankful to the members of Bioprocess Engineering Laboratory for their support. The author also thanks Mr. Toshiya Kimura, Mr. Yukihiro Masuda, Miss Asuka Sunahase, Miss Kayoko Ishii and Miss Yao Yang for their collaborations and support.

The author is grateful to the personnel of University of Fukui, Fukui Government, Fukui City Hall, Fukui International Association, members of Fukui-Brazil Friendship Association, Association of Families of Fukui-Immigrants, Buddhist Temple of Chicago, Fukui Association in Brazil and Fukui Association in Argentina for their kindness and support.

The author is thankful to the students and personnel from several elementary schools in Fukui prefecture, especially the students from Kamisho Elementary School in Ono-city for their kind words of encouragement.

The author wishes to express his appreciation to all the individuals whose support and friendship helped him to stay focused on this work. Mrs. Gabrielli Barlow, Mr. Yasuhiko Chimura, Mr. Humberto Kuk-hyun Choi, Miss Maren Ehlers, Miss Anelise Ehrhardt, Mr. Wang-pil Ko, Mr. Satoshi Nima, Mr. Takaaki Ogiso, Miss Kaori Okamura, Miss Paula Taguchi and Mr. Arturo Valencia are a few to name among them.

The author also wishes to express sincere thanks to Mr. Kohei Yamada for his support and encouragement.

Finally, but not least, the author is grateful to his parents and relatives for their continuous support.

친절하게 대해 주셔서 감사합니다　　どうもありがとうございました

Herzlichen Dank　　Muito obrigado!

March, 2008

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